

Boron Derivatives of Polyamines:  
Borane Adducts and Cyclic Cations

By

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A DISSERTATION PRESENTED TO THE GRADUATE COUNCIL OF  
THE UNIVERSITY OF FLORIDA IN PARTIAL  
FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF  
DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA  
1976

## ACKNOWLEDGMENTS

The author wishes to express his deepest appreciation to his Chairman, Dr. George E. Ryschkewitsch, whose guidance, enthusiasm, encouragement, and patience during the execution of this research program were of inestimable value. Dr. Ryschkewitsch was not only research supervisor, but friend, whose lending ear was always available.

The author wishes to express his gratitude to the members of his Supervisory Committee for the aid and guidance they have given, both in and out of the classroom. He is deeply indebted to his fellow graduate students and post-doctoral fellows of his research group, whose advice and direction were a constant source of encouragement.

The author is very thankful to Dr. Wallace Brey and his associates for obtaining the  $^{11}\text{B}$  nuclear magnetic resonance spectra reported in this study.

Special thanks are due Ms. Ella Levins for the typing of the first draft of this dissertation and to Ms. Eileen Dittmar for diligence, conscientiousness, and speed in the final typing of this dissertation.

The author wishes also to acknowledge Dr. Ralph K. Birdwhistell, Chairman, Department of Chemistry, University of West Florida, whose advice and support throughout his undergraduate and graduate studies

were of inestimable value.

Finally, the author would like to express his deepest thanks to his parents for their support and encouragement throughout the course of his college education.

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Abstract of Dissertation Presented to the Graduate Council  
of the University of Florida in Partial Fulfillment of  
the Requirements for the Degree of Doctor of Philosophy

Boron Derivatives of Polyamines:  
Borane Adducts and Cyclic Cations

By

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December, 1976

Chairman: George E. Ryschkewitsch  
Major Department: Chemistry

Two areas of polyamine chemistry were investigated. The first deals with a new synthetic method for the synthesis of 2,2'-dipyridylmethane and various derivatives. The second describes a new synthetic method, employing polyamines, for the synthesis of cyclic boronium cations, cyclic boronium cations containing an amine-borane group, and reactions and derivatives of the cyclic boronium cation derived from 2,2'-dipyridylmethane.

The diamines 2,2'-dipyridylmethanol, 2,2'-dipyridylchloromethane, and 2,2'-dipyridylmethane were obtained from the three step reaction of 2,2'-dipyridylketone with aqueous sodium borohydride, tri-n-octylphosphine and carbon tetrachloride, and powdered zinc in aqueous acid, respectively. Reaction of 2,2'-dipyridylmethane and 2,2'-dipyridylchloromethane with aqueous ammonium hexafluorophosphate provided ammonium (1+) salts. The triamine 2,2',2''-tripyridylmethane



was obtained from the reaction of 2,2'-dipyridylmethane with phenyl lithium and 2-bromopyridine.

Reaction of polyamine-boranes of tertiary aliphatic, tertiary aromatic, or mixed (aromatic, aliphatic) polyamines with iodine or trimethylamine-iodoborane results in high yields of cyclic boronium cations. The reaction is highly selective for cyclic cation formation, with no linear cation formation observed. The general utility of this method has been demonstrated with sixteen polyamine-boranes containing various combinations of aliphatic and aromatic amines.

The polyamine-boranes investigated showed a definite trend in reactivity. The rate of reaction was found to be dependent on the type of amine, and the ring size of the resulting cation. Reactivity followed the general orders: aromatic polyamine-boranes > mixed (aromatic, aliphatic) > polyamine-boranes > aliphatic polyamine-boranes, and five-membered rings > six-membered rings > seven-membered rings. The order of reactivity for various ring sizes provided a high degree of selectivity in cation formation.

When tris(boranes), derived from either symmetrical or unsymmetrical tertiary triamines, were reacted with iodine or trimethylamine-iodoborane, selective ring closure was observed. The cations obtained represent a new class of boronium cation, in which an amine-borane group ( $N-BH_3$ ) is also present in the molecule.

The cyclic boronium cation derived from 2,2'-dipyridylmethane exhibits an enhanced reactivity of the bridging

methylene hydrogens toward proton loss. The enhanced reactivity is attributed to the inductive effect of the boryl ( $\text{BH}_2^+$ ) group. Abstraction of a proton from the cation ( $K_a = 12.13$ ) resulted in the isolation of a stable zwitterion whose reactivity toward electrophilic reagents provided a means by which additional functionality could be incorporated into the amine under mild conditions.

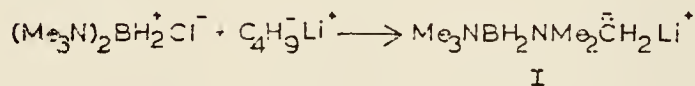
All new compounds were satisfactorily characterized by their elemental analysis, proton nmr spectrum, and infrared spectrum.

## CHAPTER I

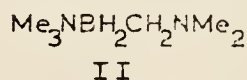
### INTRODUCTION

The chemistry of boron-nitrogen compounds, especially that of boron cations derived from tertiary amines, has grown rapidly over the past decade.<sup>1</sup> Interest in these cations, however, has concentrated mainly around reactions of the boron center and only a meager amount of work has been described concerning reactions of the coordinated amines.<sup>2-4</sup>

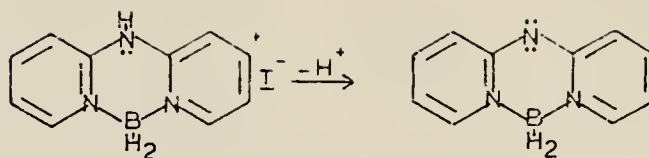
Miller and Muettterties have described the formation of a charge-compensated carbanion (I) by the abstraction of a proton from bis(trimethylamine)boronium chloride with butyllithium.<sup>2</sup>



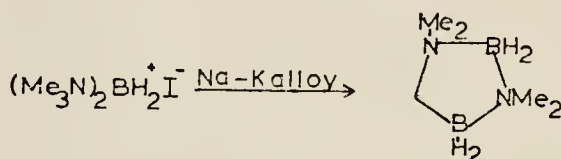
This then rearranges by either an intra- or inter-molecular process to form (trimethylamine-borylmethyl) dimethylamine (II).<sup>3</sup>



Similarly, Abate has reported that the cyclic boronium cation derived from 2,2'-dipyridylamine undergoes a proton abstraction under mildly basic conditions to produce a zwitterion.<sup>4</sup>



More recently, Gragg has investigated the reduction of bis(trimethylamine)boronium iodide with sodium potassium alloy to produce a new boron heterocycle.<sup>5</sup>



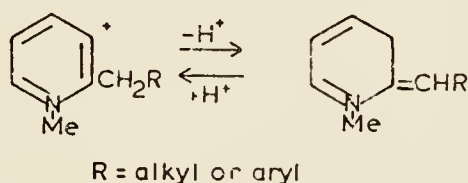
None of these reactions occur with the free amine under similar conditions. Thus, it is evident that the presence of the boryl group ( $\text{BH}_2^+$ ) enhances the reactivity of each system. It appears as if the change in chemical reactivity in the above examples correlates well with the chemistry of quaternary ammonium salts and amine adducts of Lewis acids.

The enhanced reactivities toward proton abstraction and nucleophilic substitutions of quaternary ammonium salts are well described in the literature. Such classical reactions as the Hofmann degradation, Stevens rearrangement, and ylid formation from quaternary ammonium salts are representative examples of the enhanced reactivity toward proton abstraction. Amine adducts such as pyridine N-oxides and metal complexes have also been shown to exhibit similar enhanced reactivities.

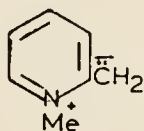
The nucleophilic substitution reactions of the pyridine system have been studied in the most detail. As the ability of the pyridine ring to undergo electrophilic attack is decreased, nucleophilic attack becomes easier. For example, the

conversion of pyridine to its proton salt increases the rate of nucleophilic substitution.<sup>6</sup>

The greater reactivity of 1-alkyl and 1-arylpyridinium salts toward nucleophilic reagents is manifested in a variety of reactions which are not possible with the free bases. One reaction that has received considerable attention is that of the formation of anhydro bases. When a quaternary pyridine bears an alkyl group in the 2 or 4 position from which a proton may be lost, the quaternary hydroxide is in equilibrium with a non-ionic base, which is formed by the removal of a proton.



Decker pointed out the structural features necessary for this conversion and some of the properties of such systems.<sup>7</sup> One such property is their behavior as carbanionic nucleophiles due to the more appreciable negative charge on the carbon atom, resulting from contribution of the following resonance structure:

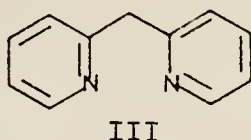


Comparison of quaternary ammonium salts to boronium salts suggest that the boryl group ( $\text{BH}_2^+$ ) would produce similar enhanced reactivity, and hence, should be considered

as an activating group for proton abstraction, and nucleophilic reactions on coordinated amines. One could also postulate that an increase in reactivity would be observed in the case of amine-borane adducts. The magnitude of this increase should not be as great as in the case of the boryl group ( $\text{BH}_2^+$ ), but should be considered since coordination of the borane to nitrogen would in effect increase the electronegativity of the nitrogen atom, thus enhancing the electrophilic character of the coordinated amine.

From the previously described chemistry of anhydrous bases, selection of a model system to investigate the enhancement of the acidity of carbon-hydrogen bonds in boronium cations was undertaken.

The model chosen was 2,2'-dipyridylmethane (III).

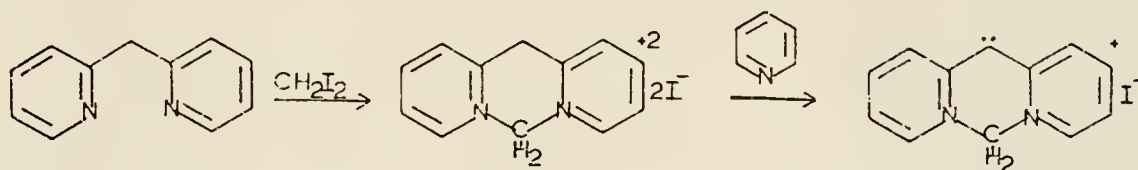


In this molecule, the acidity of the bridging methylene protons would be enhanced by the inductive effects of the nitrogen atoms and resonance delocalization of the electron pair in its conjugate base. Proton abstraction from the bridging methylene group does occur in the free amine. However, strong bases such as phenyllithium are required.

Bayer has demonstrated that zinc and cobalt(II) complexes of 2,2'-dipyridylmethane show enhanced reactivity toward proton loss.<sup>8</sup> Guckel has also shown that when 2,2'-dipyridylmethane is allowed to react with diiodomethane,

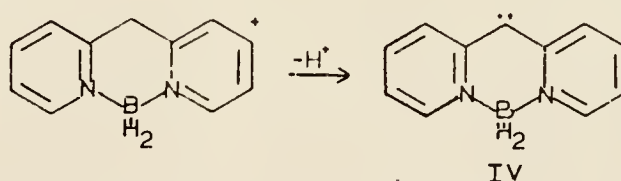


the resulting chelated quaternary ammonium ( $2^+$ ) salt undergoes reactions with weak bases, such as pyridine, to produce an intensely colored ( $1^+$ ) salt.<sup>9</sup>



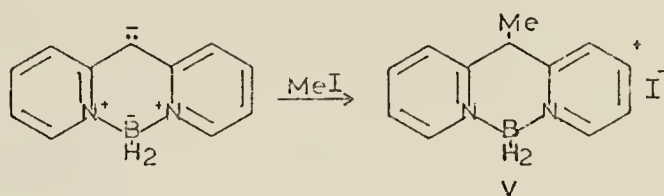
The intense color is attributed to resonance delocalization of the electron pair providing for more extended conjugation in the molecule.

The synthesis of a cyclic boronium cation, derived from 2,2'-dipyridylmethane, should produce enhanced acidity of the bridging methylene protons and the resonance delocalization of the electron pair, resulting from proton abstraction, should also provide sufficient stability for the isolation of an anhydro base (IV) derived from the boron cation.

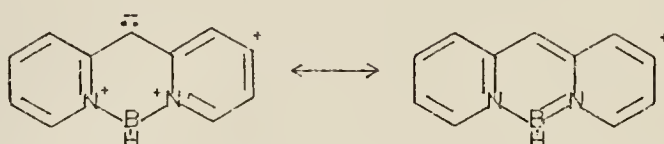


The reaction chemistry of this base (IV) toward electrophilic reagents would be of interest in light of the nucleophilic properties exhibited by other anhydro bases. The nucleophilic character would depend considerably on the extent of resonance delocalization of the electron pair. However, this reactivity, if present, would allow the incorporation of additional functionality into the boron cation which otherwise might not be possible. Thus, it might be

expected that the reaction of the anhydro base (IV), derived from the cyclic boronium cation of 2,2'-dipyridylmethane (III), with methyl iodide, would yield a methyl derivative (V).

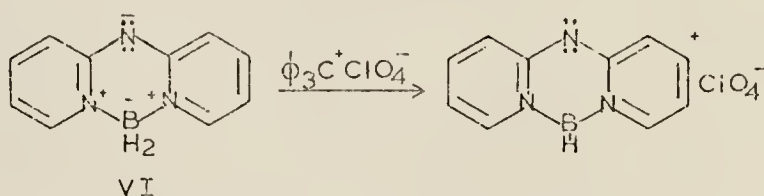


The isolation of a trigonal boron heteroaromatic system is also of interest.



No compounds of this type have yet been isolated, but evidence for their existence in solution has been reported.<sup>4,10</sup>

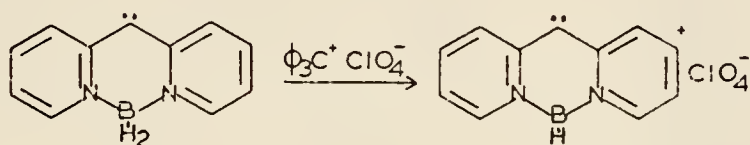
Recently Abate, in an unsuccessful attempt to isolate such a cation, reported the abstraction of a hydride ion from the anhydro base (VI), derived from the cyclic boronium cation of 2,2'-dipyridylamine, employing triphenylmethyl perchlorate.<sup>4</sup>



Although this system is quite similar to that under discussion, the replacement of the bridging nitrogen atom with a less electronegative carbon atom might provide for increased delocalization of the electron pair, hence, greater stability of the cation. Therefore, the abstraction of a hydride ion



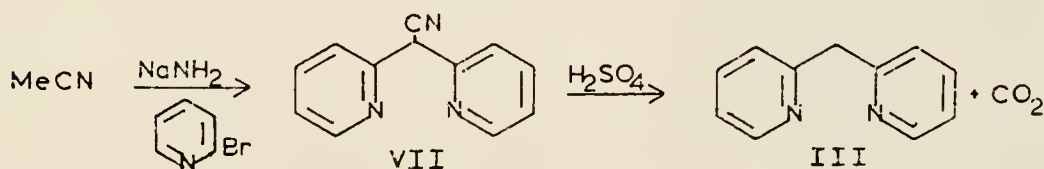
from the anhydro base of a 2,2'-dipyridylmethane boronium cation (IV), employing triphenylmethyl perchlorate, might lead to an isolable product.



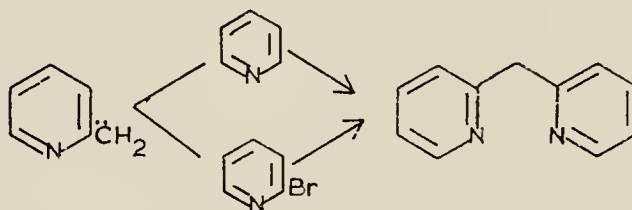
This conjugated molecule, which is homomorphic to anthracene, contains a Huckel number of electrons ( $4n+2$ ) representative of an aromatic system.

During this work, the synthesis of the cyclic boronium cation of 2,2'-dipyridylmethane appeared in the literature.<sup>11</sup> Its physical properties did not support the previous proposals for its reactivity, nor did the initial findings in this laboratory correlate with those reported. This suggested that further investigations were necessary in order to better understand the system.

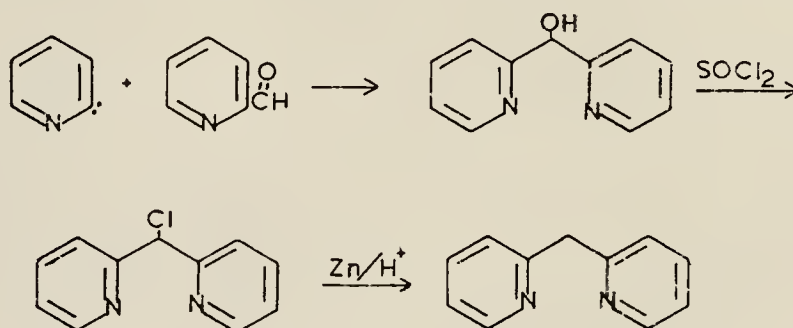
The diamine 2,2'-dipyridylmethane (III) was first synthesized in low yield by the reaction of acetonitrile, sodium amide, and 2-bromopyridine, to give dipyridyl-(2)-acetonitrile (VII), which was hydrolyzed and decarboxylated to obtain 2,2'-dipyridylmethane.<sup>12</sup>



Subsequently, it has been prepared by the reaction of 2-picolyllithium or sodium (derived from the reaction of 2-methylpyridine with either phenyllithium or sodium amide) with either pyridine or 2-bromopyridine.<sup>13-15</sup>



A multistep synthesis, starting with the preparation of 2,2'-dipyridylmethanol (VIII), has also been described.<sup>16</sup>



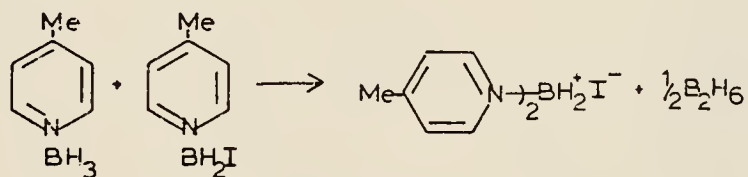
Preliminary investigations of these reported methods of synthesis suggested that they would not be useful for this study since the yields were low and the products were difficult to purify. Therefore, the investigation of a possible new synthetic route was undertaken.

The commercially available compound 2,2'-dipyridylketone could represent a convenient starting point for the synthesis of 2,2'-dipyridylmethane. It has been reported that attempts to reduce the carbonyl directly to the alkane by classical methods were unsuccessful. This is surprising, since

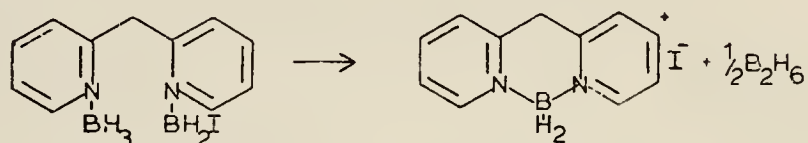
benzophenone, which is homomorphic with 2,2'-dipyridylketone, undergoes reduction easily, yielding diphenylmethane. It should be possible, however, to reduce the ketone to the alcohol and then proceed through a reaction pathway similar to that previously described.<sup>16</sup>

The synthetic methods employed for the synthesis of boron cations from tertiary amines are well described, and allow numerous variations providing considerable flexibility for their synthesis.<sup>1,17</sup> Preliminary investigations of some of the more general methods failed to produce the desired cyclic cation from 2,2'-dipyridylmethane. This was quite surprising, since the synthesis of the analogous boronium cation of 2,2'-dipyridylamine proceeded successfully by several of these methods. The failure of 2,2'-dipyridylmethane to behave as a typical diamine initiated the investigation for a new method of synthesis for the cyclic cation.

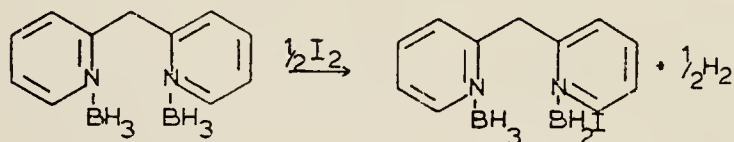
Concurrently with this work, McMaster was investigating the reaction of amine-boranes with amine-iodoboranes and observed the following:<sup>18</sup> When 4-methylpyridine-borane is allowed to react with 4-methylpyridine-iodoborane, in benzene, the products are bis-4-methylpyridine-boroniumiodide and diborane.



Comparison of the diamine 2,2'-dipyridylmethane with the starting materials and cation produced above, suggest that the two systems are structurally quite similar and that suitable conditions might exist for an intra-molecular reaction to produce the desired cation, assuming that the borane and iodoborane entities can be incorporated into the diamine.



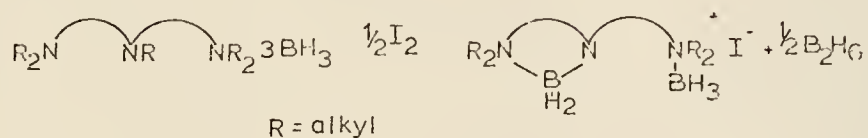
Incorporation of the borane and iodoborane entities might be accomplished by the reaction of the bis(borane) of the diamine with a stoichiometric amount of iodine necessary to iodinate only one of the borane groups.



This system would then be expected to produce the cyclic cation in a reaction analogous to that of the 4-methylpyridine system. Extension of this reaction sequence to other bis(boranes) might also provide for a new general synthetic procedure for the synthesis of cyclic boronium cations derived from diamines.

Still another interesting aspect of this proposed reaction is its possible application to tris(boranes) derived from tertiary triamines. If an amount of iodine

necessary to iodinate only one of the borane entities is employed, a new class of compounds might result, in which both a boryl ( $\text{BH}_2^+$ ) and borane ( $\text{BH}_3$ ) functionality are present in the same molecule.



This proposal was indeed found to be applicable to both bis(boranes) and tris(boranes), and provides a very general, high yield method of synthesis of cyclic boronium cations.

## CHAPTER II

### MATERIALS AND INSTRUMENTATION

#### Materials

Samples of 2,2'-dipyridylketone and 2,2'-pyridil were obtained from Aldrich Chemical Company, Inc. in 97% purity.

Sodium borohydride was obtained from Fisher Chemical Company in good purity.

The various polyamines were obtained from either Aldrich Chemical Company, Inc., Peninsular Chemical Company, or ICN Life Sciences Group (K&K), dried over Molecular Sieves 3A, and used without further purification.

Cylinder gases were obtained from Matheson Company, and were used without further purification.

Ammonium hexafluorophosphate was obtained from Ozark-Mahoning Company and was used without further purification.

Amine-boranes were obtained from Callery Chemical Company, and were used without further purification.

Methyl fluorosulfonate (Magic Methyl) was obtained from Aldrich Chemical Company, Inc. and was used without further purification.

All solvents, except 1,2-dimethoxyethane (monoglyme), supplied by various commercial sources, were used without further purification except for drying over calcium hydride or Molecular Sieves 3A. Monoglyme was treated with alumina

to remove any peroxides, stored over calcium hydride for a few days and then fractionally distilled from lithium aluminium hydride, saving the middle 80%.

### Instrumentation

Infrared spectra were obtained on a Beckman IR-10 spectrophotometer. Samples were prepared as KBr pellets. Liquid amines were run neat, if possible, using either sodium chloride or potassium bromide plates.

Proton nmr spectra were taken on a Varian A-60 instrument with tetramethylsilane as internal reference.  $^{11}\text{B}$  nmr spectra were run at 32.1 MHz with trimethylborate as an external standard.

Ultraviolet and visible spectra were obtained on a Beckman DB-G spectrophotometer using 1 cm square, fused-silica cells.

Melting points were taken on a Thomas-Hoover apparatus and were not corrected.

Elemental analyses were obtained from Galbraith Laboratories, Inc., or Atlantic Microlab, Inc.

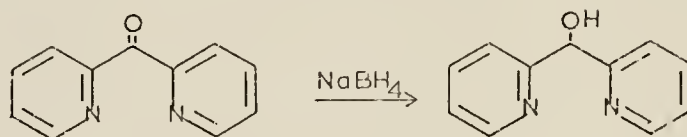
All pH measurements were taken with a Corning 12 Research pH meter with a Beckman Ag-AgCl glass electrode vs. a saturated calomel electrode.



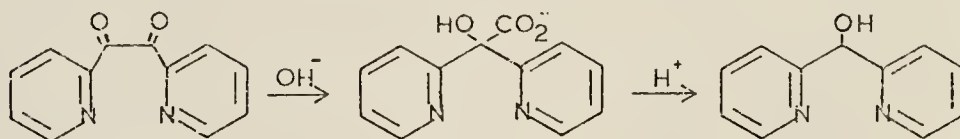
### CHAPTER III

#### SYNTHESIS OF 2,2'-DIPYRIDYLMETHANE AND DERIVATIVES

Two methods for the preparation of 2,2'-dipyridylmethanol were investigated.. The first employs the direct reduction of 2,2'-dipyridylketone with aqueous sodium borohydride.



The second method of synthesis involves a multistep approach, as described by Klosa,<sup>19,20</sup> in which 2,2'-pyridil undergoes a base promoted benzilic acid type of rearrangement. The resulting acid salt is readily decarboxylated under acidic conditions, yielding 2,2'-dipyridylmethanol.



Attempts to reproduce the reported procedure resulted in considerably lower yields than those reported. The ready availability of the starting material, however, makes this procedure attractive, especially when large quantities of 2,2'-dipyridylmethanol are desired.

Synthesis of 2,2'-dipyridylmethanol from 2,2'-dipyridylketone and aqueous sodium borohydride. A sample of 2,2'-dipyridylketone (25.0 g, 97% purity, 132 mmol) was



dissolved in  $\text{H}_2\text{O}$  (150 ml). To this solution was added  $\text{NaBH}_4$  (7.0 g, 185 mmol). The mixture was magnetically stirred for 10 hours to ensure complete reaction, and extracted with four portions (100 ml) of  $\text{CH}_2\text{Cl}_2$ . The combined  $\text{CH}_2\text{Cl}_2$  extracts were dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and the  $\text{CH}_2\text{Cl}_2$  removed under reduced pressure. The remaining brown, viscous oil was distilled under reduced pressure. The 2,2'-dipyridylmethanol obtained was a colorless, almost odorless, viscous oil, bp 106-110° at .2 mm (yield 22.5 g, 91.9%), which rapidly darkened on exposure to air. Anal. Calcd. for  $\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}$ : C, 70.99; H, 5.38; N, 15.05. Found: C, 70.02; H, 5.44; N, 14.59.

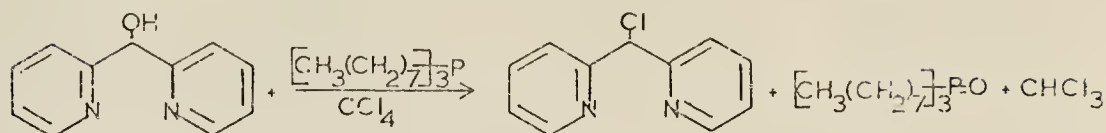
Proton nmr in  $\text{CCl}_4$ : broad doublet at -5.88 ppm, and three multiplets centered at -6.94 ppm, -7.47 ppm, and -8.37 ppm, with an intensity ratio of 2:2:4:2, respectively.

Infrared: characterized by strong absorption at  $3200\text{ cm}^{-1}$ , assigned to OH stretch, and by the absence of any carbonyl absorptions in the region  $1600\text{--}1750\text{ cm}^{-1}$ . Additional absorptions: 1590 (s), 1570 (s), 1470 (s), 1435 (s), 1400, 1310, 1210, 1150, 1100, 1050 (s, broad, structured), 860, 760 (s, broad, structured)  $\text{cm}^{-1}$ .

#### Synthesis of 2,2'-dipyridylmethanol from 2,2'-pyridil.

The synthetic procedure employed was identical to that described by Klosa.<sup>20</sup> The yield (60%), however, was considerably lower than reported (90%), for no apparent reason. The product was identical to that obtained from the aqueous sodium borohydride reduction of 2,2'-dipyridylketone.

Synthesis of 2,2'-dipyridylchloromethane.



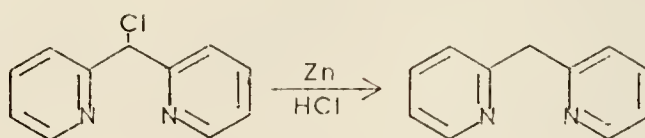
A sample of 2,2'-dipyridylmethanol (15.0 g, 80.6 mmol) was dissolved in dry  $\text{CCl}_4$  (150 ml). To this mixture, which was cooled in an ice bath, was added dropwise, tri-n-octylphosphine (44.8 g, 120.0 mmol) over a 30 minute period. Upon completion of addition, the deep red solution was stirred for three hours and extracted with four portions (100 ml) of 6N HCl. This extraction was often complicated by the formation of a gelatinous suspension. Dispersion of this suspension was accomplished by the addition of  $\text{CHCl}_3$ ; volumes required varied, but often approached 600 ml. The combined aqueous acid extracts were further extracted with two portions (100 ml) of  $\text{CH}_2\text{Cl}_2$ , to insure complete removal of any tri-n-octylphosphine or tri-n-octylphosphine oxide carried over in the initial extraction. The aqueous acid solution was cooled in an ice bath, and  $\text{CH}_2\text{Cl}_2$  (200 ml) was added. To this magnetically stirred mixture was added concentrated aqueous ammonia until the solution became alkaline (pH 11). The rate of addition was such to prevent boiling of the  $\text{CH}_2\text{Cl}_2$ . After separation of the  $\text{CH}_2\text{Cl}_2$  from the aqueous solution, the aqueous solution was further extracted with two portions (50 ml) of  $\text{CH}_2\text{Cl}_2$ . To the combined  $\text{CH}_2\text{Cl}_2$  extracts was added, with stirring, approximately 5 g of Norite (decolorizing charcoal). The mixture was filtered,

dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and the  $\text{CH}_2\text{Cl}_2$  removed under reduced pressure. The remaining brown solid was recrystallized from petroleum ether (bp 65-110°), yielding long, colorless needles, mp 73-74° (yield 14.90 g, 90.4%), which were not sensitive to air. Anal. Calcd. for  $\text{C}_{11}\text{H}_9\text{N}_2\text{Cl}$ : C, 64.54; H, 4.40; N, 13.69; Cl, 17.36. Found: C, 64.45; H, 4.46; N, 13.71; Cl, 17.36.

Proton nmr in  $\text{CCl}_4$ : singlet at -612 ppm, and three multiplets centered at -7.09 ppm, -7.60 ppm, and -8.49 ppm, with an intensity ratio of 1:2:4:2, respectively.

Infrared: absorptions at 2990, 1599 (s, broad, structured), 1540, 1478, 1310, 1150 (w), 1095 (w), 995 (s), 700 (s, broad, structured),  $595\text{ cm}^{-1}$ .

Synthesis of 2,2'-dipyridylmethane from 2,2'-dipyridylchloromethane.



A sample of 2,2'-dipyridylchloromethane (15.0 g, 73.3 mmol) was dissolved in 8N HCl (200 ml). To this solution was added slowly, zinc powder (20.0 g, 0.306 mmol). The mixture was magnetically stirred for 20 hours to insure complete reaction. The resulting solution was cooled, made alkaline by the addition of concentrated aqueous ammonia, filtered, and extracted with four portions (75 ml) of  $\text{CH}_2\text{Cl}_2$ . The combined  $\text{CH}_2\text{Cl}_2$  extracts were dried over anhydrous

$\text{Na}_2\text{SO}_4$ , filtered, and the  $\text{CH}_2\text{Cl}_2$  removed under reduced pressure. The proton nmr of the remaining brown mobile oil (11.5 g) revealed only the presence of 2,2'-dipyridylmethane. The oil was distilled under reduced pressure, yielding a pale yellow, almost odorless oil, bp  $125^\circ$  at 2 mm (yield 10.2 g, 82%), which darkened upon exposure to air. Anal. Calcd. for  $\text{C}_{11}\text{H}_{10}\text{N}_2$ : C, 77.64; H, 5.88; N, 16.47. Found: C, 77.44; H, 5.96; N, 16.49.

Proton nmr in  $\text{CCl}_4$ : sharp singlet at -4.21 ppm, and two doublets centered at -7.19 ppm, and -8.42 ppm, with an intensity ratio of 2:6:2, respectively.

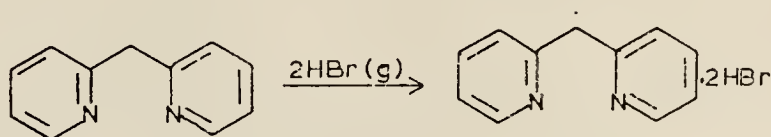
Infrared: absorptions at 3060 (w), 3000 (w), 1590 (s), 1570 (s), 1470 (s), 1432 (s), 1310 (w), 1210 (w), 1150 (w), 1100 (w), 1050 (w), 999 (s), 755 (s), 630 (w), 610 (w)  $\text{cm}^{-1}$ .

Direct synthesis of 2,2'-dipyridylmethane, starting with 2,2'-dipyridylketone. A pure sample of 2,2'-dipyridylmethane can be obtained through a continuous reaction sequence of the before-mentioned reactions, eliminating the need of isolation of each intermediate.

A sample of 2,2'-dipyridylketone (25.0 g, 97% purity, 132 mmol) was dissolved in  $\text{H}_2\text{O}$  (150 ml). To this solution was added sodium borohydride (7.0 g, 185 mmol). The mixture was magnetically stirred for 10 hours to insure complete reaction. The aqueous solution was extracted with four portions (100 ml) of  $\text{CH}_2\text{Cl}_2$ . The combined extracts were dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and the  $\text{CH}_2\text{Cl}_2$  removed under reduced pressure. To the remaining brown, viscous

oil was added dry  $\text{CCl}_4$  (200 ml). To this mixture, which was cooled in an ice bath, was added tri-n-octylphosphine (73.9 g, 198 mmol) over a one hour period. Upon completion of the addition of tri-n-octylphosphine, the resulting deep red solution was extracted with four portions (100 ml) of 6N HCl. If the extraction resulted in a gelatinous suspension,  $\text{CHCl}_3$  was added to disperse it, as described in the synthesis of 2,2'-dipyridylchloromethane. The combined aqueous acid extracts were further extracted with two portions (100 ml) of  $\text{CH}_2\text{Cl}_2$  to insure complete removal of any tri-n-octylphosphine or tri-n-octylphosphine oxide carried over in the initial extraction. To the aqueous acid solution was added slowly, zinc powder (40.0 g, 612 mmol) over a 20 minute period. The mixture was magnetically stirred for 20 hours to ensure complete reaction. The resulting solution was cooled in an ice bath, made alkaline by the addition of concentrated aqueous ammonia, filtered, and extracted with four portions (150 ml) of  $\text{CH}_2\text{Cl}_2$ . The combined  $\text{CH}_2\text{Cl}_2$  extracts were dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and the  $\text{CH}_2\text{Cl}_2$  removed under reduced pressure. The remaining brown oil was distilled under reduced pressure. The 2,2'-dipyridylmethane obtained was a pale yellow mobile oil, bp  $125^\circ$  at 2 mm (yield 20.5 g, 91.4%), which darkened upon exposure to air. This material was found to be identical to that of an authentic sample.

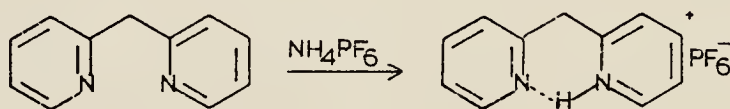
Synthesis of 2,2'-dipyridylmethane-ammonium (2+) bromide.



A sample of 2,2'-dipyridylmethane (3.00 g, 17.6 mmol), dissolved in  $\text{CH}_2\text{Cl}_2$  (300 ml), was saturated with anhydrous hydrogen bromide and magnetically stirred for one hour to ensure complete reaction. The resulting white precipitate was removed by vacuum-filtration, washed with two portions (50 ml) of diethyl ether, and vacuum-dried (yield 5.71 g, 97.4%); mp  $274^\circ$ . Anal. Calcd. for  $\text{C}_{11}\text{H}_{12}\text{N}_2(2+)$ ,  $2\text{Br}^-$ : C, 39.76; H, 3.61; N, 8.43; Br, 48.19. Found: C, 39.56; H, 3.67; N, 8.40; Br, 48.29.

Infrared: absorptions at 2600 (s, broad, structured), 1610 (s), 1535 (w), 1462 (w), 1395 (w), 1297 (s), 1222, 1159, 1090 (w), 1000 (s), 956, 923, 760 (s),  $620\text{ cm}^{-1}$ .

Synthesis of 2,2'-dipyridylmethane ammonium (1+) hexafluorophosphate.



A sample of 2,2'-dipyridylmethane (1.0 g, 5.88 mmol) was dissolved in 2N HCl (20 ml). To this solution was added 3 ml of 5M  $\text{NH}_4\text{PF}_6$  and 1N NaOH was added dropwise until the pH of the solution was 4. At this point a crystalline material formed and was removed by vacuum-filtration. The white crystalline solid was recrystallized from hot water, filtered,

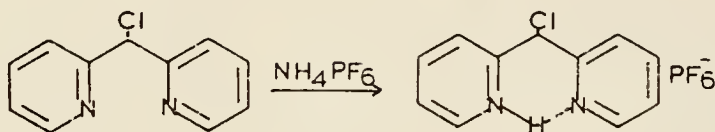


and vacuum-dried (yield 1.40 g, 75.3%); mp 95-96°. Anal. Calcd. for  $C_{11}H_{11}N_2^+$ ,  $PF_6^-$ : C, 41.77; H, 3.48; N, 8.86. Found: C, 40.89; H, 3.55; N, 8.70.

Proton nmr in  $CH_3CN$ : sharp singlet at -4.60 ppm, and three complex multiplets centered at -7.67 ppm, -8.15 ppm, and -8.31 ppm, with an intensity ratio of 2:4:2:2, respectively.

Infrared: strong absorption centered at  $2600\text{ cm}^{-1}$ , assigned to N-H stretching mode.

Synthesis of 2,2'-dipyridylchloromethane ammonium (1+) hexafluorophosphate.

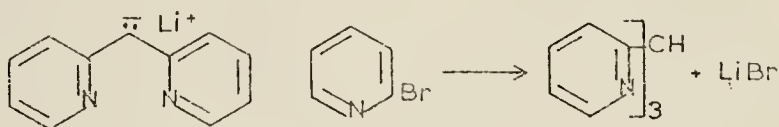


A sample of 2,2'-dipyridylchloromethane (1.0 g, 4.88 mmol) was dissolved in 2N HCl (15 ml). To this solution was added 3 ml of 5M  $NH_4PF_6$ , and 1N NaOH was added dropwise until the pH of the solution was 4. At this point, a heavy white crystalline material formed and was removed by vacuum-filtration. The white crystalline solid was recrystallized from hot water, filtered, and vacuum-dried (yield 1.50 g, 87.7%); mp 156-157°. Anal. Calcd. for  $C_{11}H_{10}ClN_2^+$ ,  $PF_6^-$ : C, 37.66; H, 2.85; N, 7.99; Cl, 10.13. Found: C, 37.77; H, 2.93; N, 8.02; Cl, 9.97.

Proton nmr in  $CH_3CN$ : sharp singlet at -6.60 ppm, and three complex multiplets centered at -7.85 ppm, -8.31 ppm, and -8.80 ppm, with an intensity ratio of 1:4:2:2, respectively.

Infrared: broad band centered at  $2900\text{ cm}^{-1}$ , assigned to the N-H stretching mode. Additional absorptions:  $1637\text{ (s)}$ ,  $1600\text{ (s)}$ ,  $1530$ ,  $1515$ ,  $1479$ ,  $1455$ ,  $1380$ ,  $1365$ ,  $1310$ ,  $1280$ ,  $1240$ ,  $1215$ ,  $1175$ ,  $1100$ ,  $1050$ ,  $1008\text{ (s)}$ ,  $845\text{ (broad, structured, assigned to PF}_6^-)$ ,  $770$ ,  $740$ ,  $703$ ,  $650\text{ (s)}$ ,  $622$ ,  $550\text{ (s)}$ ,  $485\text{ cm}^{-1}$ .

Synthesis of 2,2',2''-tripyridylmethane from 2,2'-dipyridyl-lithium and 2-bromopyridine.



Phenyl lithium was prepared by dropping bromobenzene (4.00 ml, 40.0 mmol), in anhydrous diethyl ether (25 ml), onto lithium chips (0.560 g, 80.7 mmol), suspended in anhydrous diethyl ether (200 ml), in an inert atmosphere of nitrogen. After stirring for two hours, all the lithium had dissolved, and 2,2'-dipyridylmethane (6.70 g, 39.0 mmol), in anhydrous diethyl ether (30 ml), was slowly added. Stirring was continued for one-half hour, during which time the mixture became orange in color. To this orange solution was added 2-bromopyridine (6.32 g, 40.0 mmol), dissolved in anhydrous diethyl ether (30 ml). The solution was refluxed for 45 minutes to ensure complete reaction, and poured onto crushed ice (200-300 g). The phases were separated and the aqueous layer was extracted with three portions (100 ml) of  $\text{CH}_2\text{Cl}_2$ . The ether and  $\text{CH}_2\text{Cl}_2$  solutions were combined, dried over



anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and the volatiles removed under reduced pressure. The remaining brown solid was recrystallized from hot heptane. The 2,2',2''-tripyridylmethane obtained was a pale yellow, crystalline solid (yield 6.3 g, 76%); mp  $100^\circ$ , which was not air sensitive. Anal. Calcd. for  $\text{C}_{16}\text{H}_{13}\text{N}_3$ : C, 77.73; H, 5.26; N, 17.00. Found: C, 77.69; H, 5.30; N, 16.92.

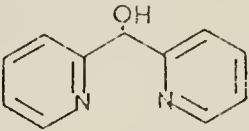
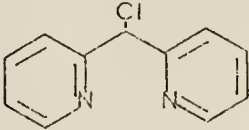
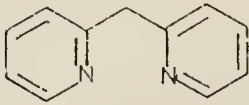
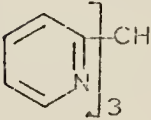
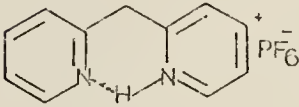
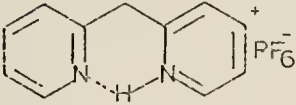
Proton nmr in  $\text{CCl}_4$ : sharp singlet at -5.81 ppm, and two complex multiplets centered at -7.25 ppm, -8.40 ppm, with an intensity ratio of 1:9:3, respectively.

Infrared: absorptions at 3060 (w), 1593 (s), 1575 (w), 1470 (w, structured), 1439 (s), 1151 (w), 1090 (w), 1050 (w), 996 (w), 786 (w), 752 (s)  $\text{cm}^{-1}$ .

The yields, melting points, and boiling points of all compounds in this chapter appear in Table I.

Table I

Yields, Melting and Boiling Points of  
2,2'-Dipyridylmethane and Derivatives

Compound	Yield %	Mp °C	Bp °C	Lit
	91.9		106-110 .2mm	----
	90.4	73-74		----
	82.0		125 .2mm	126-132 <sup>a</sup> 5mm
	76.0	100		100-101 <sup>a</sup>
	75.3	95-96		----
	87.7	156-159		----

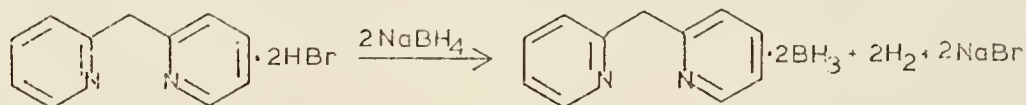
<sup>a</sup> C. Osuch and R. Levine, J. Am. Chem. Soc., **78**, 1723(1956)

## CHAPTER IV

### SYNTHESIS OF POLYAMINE-BORANES

Borane adducts of polyamines containing two or more tertiary nitrogen atoms, are prepared by three apparently general synthetic methods.<sup>21-24</sup> These syntheses proceed from (1) sodium borohydride and acid salts of polyamines, (2) trimethylamine-borane and polyamine, or (3) sodium borohydride, iodine and polyamine. The general procedures and usefulness of each synthetic method are illustrated, and referred to as general procedures 1, 2, and 3, respectively, in the description of synthesis of various polyamine-boranes. New polyamine-boranes were satisfactorily characterized by elemental analysis, and their infrared and proton nmr spectra.

#### Synthesis of 2,2'-dipyridylmethane-bis(borane).



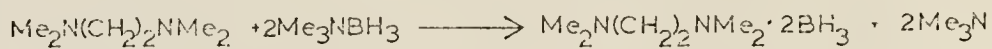
To a magnetically stirred slurry of 2,2'-dipyridylmethane-ammonium (2<sup>+</sup>) bromide (2.39 g, 7.20 mmol), in dry peroxide-free 1,2-dimethoxyethane (100 ml), was added sodium borohydride (94% hydride purity, 0.606 g, 16.0 mmol, 10% excess). Vigorous evolution of hydrogen ensued, and stirring was continued for two hours or until hydrogen evolution ceased. The volatiles were removed under reduced pressure, and the re-

remaining white solid was extracted with two portions (20 ml) of  $\text{CH}_2\text{Cl}_2$  to remove the soluble bis(borane) from sodium bromide and unreacted sodium borohydride. The two  $\text{CH}_2\text{Cl}_2$  extracts were combined and hexane (150 ml) was added, producing a white precipitate. This material was removed by vacuum-filtration, and vacuum-dried (yield 1.32 g, 92.3%); mp  $145^\circ$ , (turns red at  $130^\circ$  and melts with decomposition at  $145^\circ$ ). Anal. Calcd. for  $\text{C}_{11}\text{H}_{15}\text{B}_2\text{N}_2$ : C, 66.66; H, 8.08; N, 14.14; B, 11.12. Found: C, 66.39; H, 8.22; N, 13.93; B, 11.29.

Proton nmr in  $\text{CDCl}_3$ : sharp singlet at  $-3.49$  ppm, and three complex multiplets centered at  $-7.29$  ppm,  $-7.88$  ppm, and  $-8.82$  ppm, with an intensity ratio of 2:4:2:2, respectively.

Infrared: strong absorption centered at  $2350\text{ cm}^{-1}$ , assigned to B-H stretching mode. Additional absorptions: 1626 (s), 1580 (w), 1590 (s, broad, structured), 1452, 1440, 1420, 1189 (s), 1162 (s), 1110, 1089, 935, 762 (s)  $\text{cm}^{-1}$ .

Synthesis of N,N,N',N'-tetramethylethanediamine-bis(borane).



Trimethylamine-borane (8.07 g, 111 mmol) and freshly distilled N,N,N',N'-tetramethylethanediamine (6.47 g, 55.6 mmol) were combined with benzene (30 ml) in an Erlenmeyer flask (50 ml) fitted with a reflux condenser and a T-adaptor, through which nitrogen gas was passed to remove liberated trimethylamine.

The mixture was magnetically stirred and heated in an oil bath at 80° for 6 hours, with continuous nitrogen flushing. To the mixture, containing a white solid, was added petroleum ether (50 ml). The solution was vacuum-filtered, and the solid placed in a vacuum sublimator and pumped on overnight. Bis(borane) (7.55 g, 52.5 mmol, yield 93%) was recovered, mp 183°, lit.,<sup>25-27</sup> 182.5-185°.

The proton nmr and infrared spectra were identical to those previously reported.<sup>25-27</sup>

Synthesis of 2-(2-N-piperidinoethyl)pyridine-bis(borane).



Sodium borohydride (2.19 g, 57.9 mmol, 10% excess) and 2-(2-N-piperidinoethyl)pyridine (500 g, 26.3 mmol) were suspended in dry monoglyme (60 ml) in a two-neck flask (250 ml), fitted with a pressure-compensating dropping funnel, and outlet tube leading to a bubbler containing a benzene-amine mixture, as described by Nainan.<sup>28</sup> To this slurry was added dropwise, iodine (6.70 g, 26.4 mmol), dissolved in monoglyme (40 ml), over a one hour period. The mixture was stirred throughout the reaction, while hydrogen gas escaped through the bubbler. The solvent was removed under vacuum, and the resulting solid was extracted with dry CH<sub>2</sub>Cl<sub>2</sub> (100 ml) to separate the soluble amine-borane from sodium iodide and unreacted borohydride. The CH<sub>2</sub>Cl<sub>2</sub> was removed under vacuum, and the remaining

solid was washed with water (50 ml) to remove any sodium iodide that was solubilized by the borane. The product was vacuum-dried for 10 hours (yield 5.36 g, 93.3%); mp 105°.

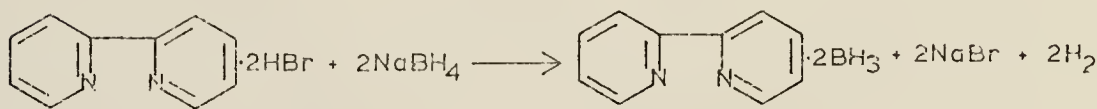
Anal. Calcd. for  $C_{12}H_{24}B_2N_2$ : C, 66.06; H, 11.01; N, 12.84.

Found: C, 65.83; H, 10.88; N, 12.56.

Proton nmr in  $CH_2Cl_2$ : six complex multiplets centered at -1.67 ppm, -3.00 ppm, -3.70 ppm, -7.38 ppm, -7.89 ppm, and -8.65 ppm, with an intensity ratio of 6:4:4:2:1:1, respectively.

Infrared: strong absorption centered at  $2320\text{ cm}^{-1}$ , assigned to the B-H stretching mode. Additional absorptions: 2900 (s, broad, structured), 1619 (w), 1576 (w), 1489 (s), 1472, 1445 (s), 1180 (s, broad, structured), 1116 (w), 1080 (w), 1025 (w), 972, 760 (s)  $\text{cm}^{-1}$ .

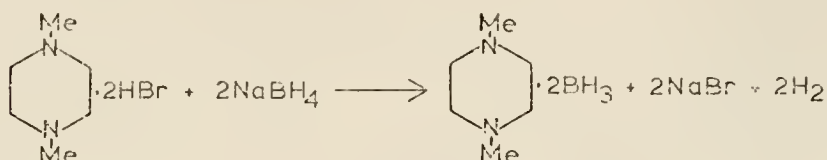
Synthesis of 2,2'-dipyridyl-bis(borane).



A sample of 2,2'-dipyridyl-ammonium (2+) bromide (9.4014 g, 29.6 mmol) was reacted with sodium borohydride (2.46 g, 65.1 mmol, 10% excess), according to procedure (1). After removal of the volatiles, the remaining solid was washed with water (50 ml). The insoluble bis(borane), a white crystalline solid, was collected by vacuum-filtration, and vacuum-dried overnight (yield 4.80 g, 88.2%). The compound does not melt up to 300°, as reported.<sup>22</sup>

The proton nmr and infrared spectra were identical to those of an authentic sample.

Syntheses of N,N'-dimethylpiperazine-bis(borane).



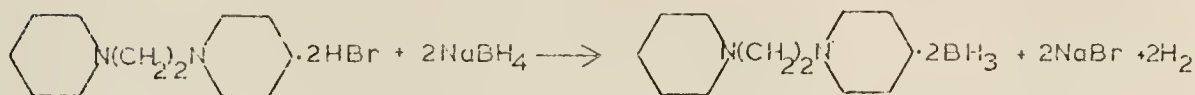
A sample of N,N'-dimethylpiperazine-ammonium (2+) bromide (17.0 g, 61.6 mmol) was reacted with sodium borohydride (5.83 g, 154 mmol, 10% excess), according to procedure (1). After removal of the volatiles a white crystalline solid remained, which was redissolved in  $\text{CH}_2\text{Cl}_2$  (30 ml) and precipitated by the addition of hexane. The bis(borane) obtained was vacuum-dried for five hours (yield 8.02 g, 91.7%) mp  $179^\circ$ . Anal. Calcd. for  $\text{C}_6\text{H}_{20}\text{B}_2\text{N}_2$ : C, 50.70; H, 14.08; N, 19.72. Found: C, 50.63; H, 14.27; N, 19.68.

Proton nmr in  $\text{CH}_2\text{Cl}_2$ : broad singlet at -2.17 ppm, and a complex multiplet shouldering this singlet centered at -3.10 ppm, with an intensity ratio of 6:8, respectively.

Infrared: strong absorption centered at  $2350\text{ cm}^{-1}$ , assigned to the B-H stretching mode. Additional absorptions: 3110 (w), 2960 (w), 2090 (w), 1450 (s, structured), 1330, 1300 (s), 1190 (s), 1150 (s, doublet), 1120 (s), 1100, 1032 (s), 990 (s), 995 (s), 859 (s)  $\text{cm}^{-1}$ .



Synthesis of 1,2(N,N'-bis-piperidine)ethane-bis(borane).

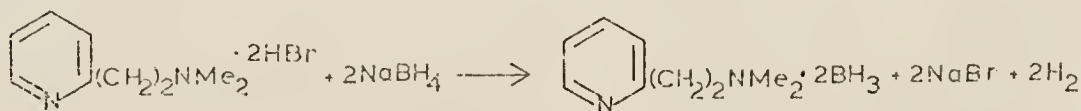


A sample of 1,2(N,N'-bis-piperidine)ethane-ammonium (2+) bromide (19.5 g, 56.0 mmol) was reacted with sodium borohydride (5.30 g, 140 mmol, 20% excess) according to procedure (1). The product was collected by vacuum-filtration, and vacuum-dried for 10 hours (yield 10.1 g, 47.2 mmol, 84.3% of bis(borane)); mp 205°. Anal. Calcd. for  $\text{C}_{12}\text{H}_{30}\text{B}_2\text{N}_2$ : C, 64.29; H, 13.39; N, 12.50. Found: C, 64.23; H, 13.53; N, 12.49.

Proton nmr in  $\text{CH}_2\text{Cl}_2$ : two broad complex multiplets and a singlet centered at -1.66 ppm, -2.83 ppm, and -3.14 ppm, with an intensity ratio of 12:8:4, respectively.

Infrared: strong absorption centered at  $2350\text{ cm}^{-1}$ , assigned to the B-H stretching mode. Additional absorptions: 2960 (s), 2940 (s), 1480, 1449 (s), 1409 (w), 1331 (s), 1300 (s), 1275 (w), 1190 (s), 1180 (s), 1150 (s), 1082 (s), 1040 (s), 980 (s), 954 (s), 910 (s), 860 (s), 810 (w), 772 (s)  $\text{cm}^{-1}$ .

Synthesis of 2-(2-dimethylaminoethyl) pyridine-bis(borane).



A sample of 2-(2-dimethylaminoethyl) pyridine-ammonium (2+) bromide (5.0 g, 16.0 mmol) was reacted with sodium borohydride

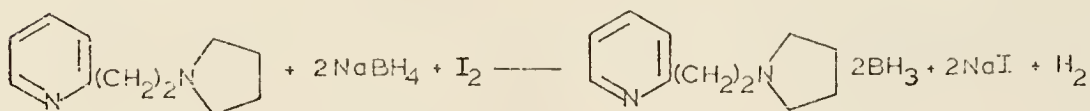


(1.40 g, 40.0 mmol, 20% excess) according to procedure (1). After removal of the volatiles, the remaining white solid was redissolved in  $\text{CH}_2\text{Cl}_2$  (25 ml) and precipitated by addition of hexane. The bis(borane) obtained was vacuum-dried for five hours (yield 2.40 g, 84.3%); mp  $100^\circ$ . Anal. Calcd. for  $\text{C}_9\text{H}_{20}\text{B}_2\text{N}_2$ : C, 60.67; H, 11.24; N, 15.73. Found: C, 60.81; H, 11.44; N, 15.62.

Proton nmr in  $\text{CH}_2\text{Cl}_2$ : sharp singlet at  $-2.65$  ppm, and five complex multiplets centered at  $-3.08$  ppm,  $-3.65$  ppm,  $-7.48$  ppm,  $-7.90$  ppm, and  $-8.67$  ppm, with an intensity ratio of 6:2:2:2:1:1, respectively.

Infrared: strong absorption centered at  $2330\text{ cm}^{-1}$ , assigned to the B-H stretching mode. Additional absorptions:  $1620$  (w),  $1578$  (w),  $1462$  (s, broad, structured),  $1319$ ,  $1170$  (s, broad, structured),  $1100$  (w),  $1092$  (w),  $1035$ ,  $1015$ ,  $990$ ,  $930$ ,  $840$  (w),  $820$  (w),  $765$  (s)  $\text{cm}^{-1}$ .

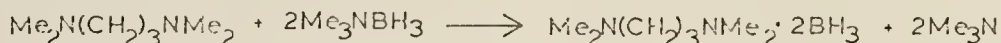
Synthesis of 2-(2-N-pyrrolidinoethyl)pyridine-bis(borane).



A sample of 2-(2-N-pyrrolidinoethyl)pyridine (5.0 g, 28.4 mmol), was reacted with sodium borohydride (2.47 g, 65.3 mmol, 15% excess) and iodine (7.2 g, 28.4 mmol) according to procedure (3). After removal of the volatiles, the white solid was extracted with  $\text{CH}_2\text{Cl}_2$  (100 ml), to separate the soluble bis(borane) from sodium iodide and unreacted sodium

borohydride. The  $\text{CH}_2\text{Cl}_2$  was removed under vacuum, and the solid was washed with water (50 ml) to remove any sodium iodide that was solubilized by the borane. The product was vacuum-dried for 10 hours (yield 5.35 g, 92.4%); mp  $96^\circ$ . Anal. Calcd. for  $\text{C}_{11}\text{H}_{22}\text{B}_2\text{N}$ : C, 64.71; H, 10.78; N, 13.73. Found: C, 64.50; H, 10.68; N, 13.62.

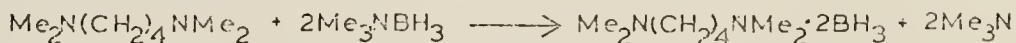
Synthesis of N,N,N',N'-tetramethyl-1,3-propanediamine-bis(borane).



Samples of N,N,N',N'-tetramethyl-1,3-propanediamine (7.25 g, 55.6 mmol) and trimethylamine-borane (8.04 g, 110 mmol) were reacted according to procedure (2) for 30 hours. A white solid was collected (yield 7.95 g, 90.3%); mp  $145^\circ$ , lit.<sup>26,27</sup>  $144\text{--}145^\circ$ .

The proton nmr and infrared spectra were identical to those of an authentic sample.

Synthesis of N,N,N',N'-tetramethyl-1,4-butanediamine-bis(borane).

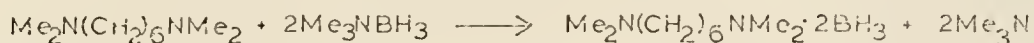


Samples of N,N,N',N'-tetramethyl-1,4-butanediamine (4.35 g, 30.2 mmol) and trimethylamine-borane (4.24 g, 58.0 mmol) were reacted according to procedure (2) for 30 hours. A white solid was collected (yield 4.34 g, 87.9%); mp  $151^\circ$ ,

lit.<sup>26,27</sup> 147-149°.

The proton nmr and infrared spectra were identical to those of an authentic sample.

Synthesis of N,N,N',N'-tetramethyl-1,6-hexanediamine-bis(borane).

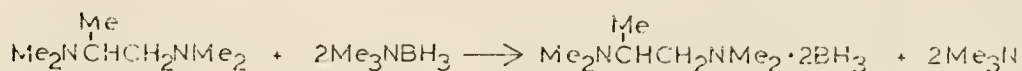


Samples of N,N,N',N'-tetramethyl-1,6-hexanediamine (4.95 g, 28.8 mmol) and trimethylamine-borane (4.38 g, 60.0 mmol) were reacted according to procedure (2) for 30 hours. A white solid was collected (yield 5.15 g, 89.4%); mp 103°.

Proton nmr in  $\text{CH}_2\text{Cl}_2$ : two complex multiplets, one of which overlapped a broad singlet. The chemical shift of this multiplet could not be assigned exactly, due to this overlap. The upfield multiplet and singlet were centered at -1.57 ppm, and -2.52 ppm.

Infrared: strong absorption centered at  $2320\text{ cm}^{-1}$ , assigned to the B-H stretching mode. Additional absorptions: 2950 (s, broad, structured), 1470 (broad doublet), 1410, 1392, 1250, 1230, 1190 (s), 1168 (s), 1140, 1062, 1015, 991 (w), 971 (s), 870 (s), 792,  $730\text{ cm}^{-1}$ .

Synthesis of N,N,N',N'-tetramethyl-1,2-propanediamine-bis(borane).

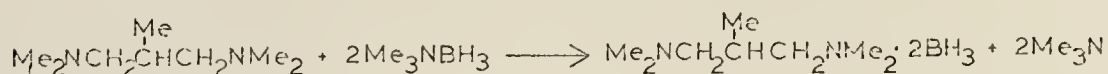


Samples of N,N,N',N'-tetramethyl-1,2-propanediamine (5.20 g,

40.0 mmol) and trimethylamine-borane (6.21 g, 85.1 mmol) were reacted according to procedure (2) for 40 hours. A white solid was collected (yield 5.72 g, 90.5%); mp 116°. Anal. Calcd. for  $C_7H_{24}B_2N_2$ : C, 53.16; H, 15.19; N, 17.72. Found: C, 53.22; H, 15.34; N, 17.81.

Proton nmr in  $CH_2Cl_2$ : doublet, two broad singlets, and a complex multiplet system encompassing the two singlets. The doublet was centered at -1.55 ppm, and the two singlets at -2.48 ppm, and -2.65 ppm.

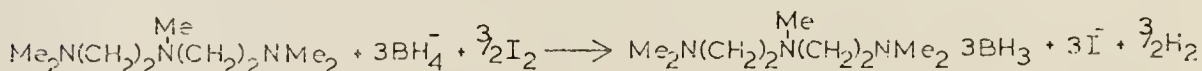
Synthesis of N,N,N',N'-2-pentamethyl-1,3-propanediamine-bis(borane).



Samples of N,N,N',N'-2-pentamethyl-1,3-propanediamine (4.00 g, 27.7 mmol) and trimethylamine-borane (5.06 g, 69.3 mmol) were reacted according to procedure (2) for 40 hours. A white solid was collected (yield 3.80 g, 79.8%); mp 96°. Anal. Calcd. for  $C_8H_{26}B_2N_2$ : C, 55.81; H, 15.12; N, 16.28. Found: C, 55.72; H, 15.21; N, 16.37.

Proton nmr in  $CD_3CN$ : sharp singlet at -2.60 ppm, a poorly resolved doublet centered at -2.07 ppm, and a complex multiplet underneath the singlet centered at approximately -2.67 ppm.

Synthesis of Pentamethyldiethylenetriamine-tris(borane).

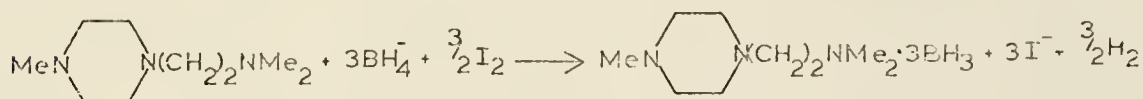


Samples of pentamethyldiethylenetriamine (1.00 g, 57.7 mmol),

sodium borohydride (7.53 g, 199 mmol, 15% excess) and iodine (22.0 g, 86.6 mmol) were reacted according to procedure (3). After removal of the volatiles, the white solid was extracted with three portions (100 ml) of water to remove any unreacted sodium borohydride and sodium iodide, vacuum-dried, and recrystallized from hot acetone (yield 10.0 g, 81.4%); mp 185°, lit.<sup>28-30</sup> 185-186°. Anal. Calcd. for  $C_9H_{31}B_3N_3$ : C, 50.23; H, 14.88; N, 19.53. Found: C, 50.35; H, 14.21; N, 19.86.

The proton nmr and infrared spectra were identical to those previously reported.<sup>28-30</sup>

Synthesis of N-methyl-N'-(2-dimethylaminoethyl)piperazine-tris(borane).

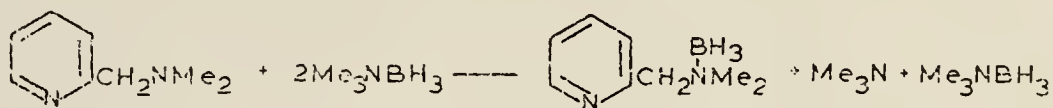


Samples of N-methyl-N'-(2-dimethylaminoethyl)piperazine (5.00 g, 29.2 mmol), sodium borohydride (3.81 g, 101 mmol, 15% excess), and iodine (11.1 g, 43.9 mmol) were reacted according to procedure (3). After removal of the volatiles, the remaining white solid was washed with three portions (50 ml) of water to remove unreacted sodium borohydride and sodium iodide, and vacuum-dried (yield 5.83g, 93.6%); mp 165°. Anal. Calcd. for  $C_9H_{30}B_3N_3$ : C, 50.70; H, 14.08; N, 19.72. Found: C, 50.88; H, 14.23; N, 19.83.

Proton nmr in  $\text{CH}_2\text{Cl}_2$ : broad singlet at -2.64 ppm, and two complex multiplets centered at -2.84 ppm, and -3.42 ppm. Due to the overlap of absorptions, definitive integration was not possible.

Infrared: strong absorption centered at  $2350\text{ cm}^{-1}$ , assigned to B-H stretching mode. Additional absorptions: 1460 (s), 1405 (w), 1345 (w), 1330, 1298, 1200 (s), 1187 (s), 1162 (s), 1137, 1112, 1082, 1017, 990 (s), 965, 928, 897, 869 (s), 841, 828, 802, 780,  $600\text{ cm}^{-1}$ .

Synthesis of 2-(trihydroborondimethylaminomethyl)pyridine.



Samples of 2-(dimethylaminomethyl)pyridine (2.50 g, 18.4 mmol) and trimethylamine-borane (1.83g, 2.50 mmol) were reacted according to procedure (2) for 30 hours. A white solid was collected (yield 2.25 g, 81.5%); mp  $55^\circ$ . Anal. Calcd. for  $\text{C}_8\text{H}_{15}\text{BN}_2$ : C, 64.00; H, 10.00; N, 18.66. Found: C, 63.84; H, 10.30; N, 18.67.

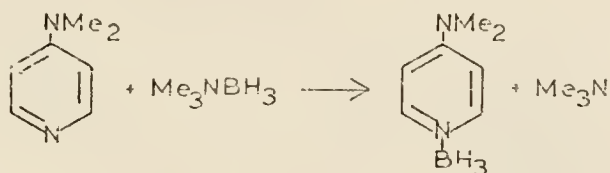
Proton nmr in  $\text{CH}_2\text{Cl}_2$ : two singlets centered at -2.60 ppm, and -4.03 ppm, and three complex multiplets centered at -7.30 ppm, -7.71 ppm, and -8.60 ppm, with an intensity ratio of 6:2:2:1:1, respectively.

Infrared: strong absorption centered at  $2340\text{ cm}^{-1}$ , assigned to B-H stretching mode. Additional absorptions: 3020 (s), 2985 (s), 2080, 1600 (s), 1580 (s), 1472 (s),



1440 (s), 1412, 1365, 1337, 1295, 1230, 1212, 1179 (s),  
1150 (s), 1140 (s), 1112, 1090, 1060, 1020 (s), 1000 (s),  
980, 940, 910, 870 (s), 826 (s), 769 (s), 759 (s), 702 (s),  
610, 510 (s), 440, 411 (s), 370  $\text{cm}^{-1}$ .

Synthesis of 4(N,N-dimethylamino)pyridine-borane.



Samples of 4-(N,N-dimethylamino)pyridine (3.00 g, 246 mmol) and trimethylamine-borane (2.69 g, 3.69 mmol) were reacted according to procedure (2) for 30 hours. A white solid was collected (yield 3.03 g, 90.7%); mp 169°. Anal. Calcd. for C<sub>7</sub>H<sub>13</sub>BN<sub>2</sub>: C, 61.76; H, 9.56; N, 20.58. Found: C, 62.50; H, 9.81; N, 20.55.

Proton nmr in CH<sub>2</sub>Cl<sub>2</sub>: sharp singlet at -3.03 ppm, and two complex multiplets centered at -6.46 ppm, and -7.93 ppm, with an intensity ratio of 6:2:2, respectively.

Infrared: strong absorption at 2300  $\text{cm}^{-1}$ , assigned to B-H stretching mode. Additional absorptions: 2938 (w), 1640 (s), 1550 (s), 1450 (s), 1398 (s), 1346, 1310, 1230 (s), 1178 (s), 1130, 1100 (s), 1068, 1040, 943, 812 (s), 512 (s), 486  $\text{cm}^{-1}$ .

The yields and melting points of all polyamine-boranes contained in this chapter appear in Table II.



Table II  
Yields and Melting Points of Polyamine-Boranes

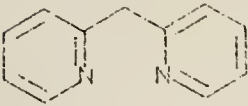

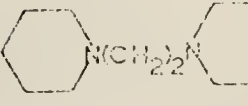
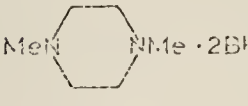

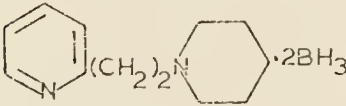
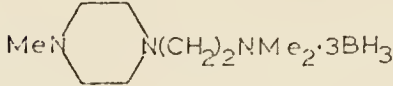
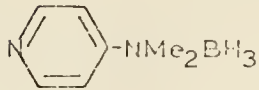
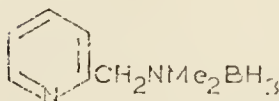
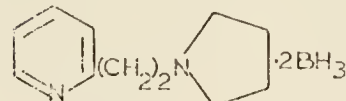
Compound	Yield %	Mp °C	Lit
$\text{Me}_2\text{N}(\text{CH}_2)_2\text{NMe}_2 \cdot 2\text{BH}_3$	93.0	183	182.5–185 <sup>a, b</sup>
$\text{Me}_2\text{N}(\text{CH}_2)_3\text{NMe}_2 \cdot 2\text{BH}_3$	90.3	146	144–145 <sup>b, c</sup>
$\text{Me}_2\text{N}(\text{CH}_2)_4\text{NMe}_2 \cdot 2\text{BH}_3$	87.0	151	147–149 <sup>b, c</sup>
$\text{Me}_2\text{N}(\text{CH}_2)_6\text{NMe}_2 \cdot 2\text{BH}_3$	89.4	103	-----
$\text{Me}_2\text{NCH}_2\overset{\text{Me}}{\underset{ }{\text{CH}}}\text{CH}_2\text{NMe}_2 \cdot 2\text{BH}_3$	79.8	96	-----
$\text{Me}_2\text{N}\overset{\text{Me}}{\underset{ }{\text{CH}}}\text{CH}_2\text{NMe}_2 \cdot 2\text{BH}_3$	90.5	116	-----
$\text{Me}_2\text{N}(\text{CH}_2)_2\overset{\text{Me}}{\underset{ }{\text{N}}}(\text{CH}_2)_2\text{NMe}_2 \cdot 3\text{BH}_3$	81.4	185–186	185–186 <sup>d, e, f</sup>
 $\cdot 2\text{BH}_3$	92.3	145	-----
 $\cdot 2\text{BH}_3$	88.2	300	300 <sup>g</sup>
 $\cdot 2\text{BH}_3$	84.3	205	-----
 $\cdot 2\text{BH}_3$	91.7	179	-----
 $(\text{CH}_2)_2\text{NMe}_2 \cdot 2\text{BH}_3$	94.3	100	-----

Table II (continued)

Compound	Yield %	Mp °C	Lit
 <chem>C1=CC=CC=C1N(CCC1CCCCC1)B(B)B</chem>	93.3	105	----
 <chem>CN1CCCCC1N(CCCN(C)C)B(B)B</chem>	93.6	165	----
 <chem>CN(C)CCc1ccncc1B(B)B</chem>	90.7	169	----
 <chem>CN(C)CCc1ccncc1B(B)B</chem>	81.5	55	----
 <chem>C1=CC=CC=C1N(CCC1CCCC1)B(B)B</chem>	92.4	96	----

<sup>a</sup> N. E. Miller and E. L. Muettert, *J. Am. Chem. Soc.*, **86**, 1033(1964); <sup>b</sup> T. E. Sullivan, Doctoral Dissertation, University of Florida, (1970); <sup>c</sup> G. E. Ryschkewitsch and T. E. Sullivan, *Inorg. Chem.*, **9**, 899(1970); <sup>d</sup> K. C. Nainan, Doctoral Dissertation, University of Florida, (1969); <sup>e</sup> F. E. Walker and R. K. Pearson, *J. Inorg. Nucl. Chem.*, **27**, 1981(1965); <sup>f</sup> K. C. Nainan and G. E. Ryschkewitsch, *J. Am. Chem. Soc.*, **91**, 330(1969); <sup>g</sup> K. C. Nainan and G. E. Ryschkewitsch, *Inorg. Chem.*, **8**, 2671(1969).

## CHAPTER V

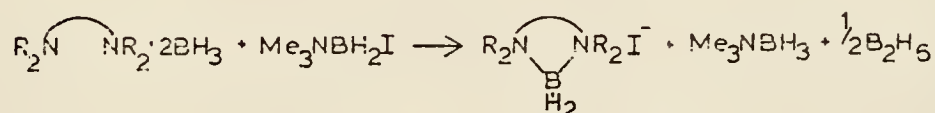
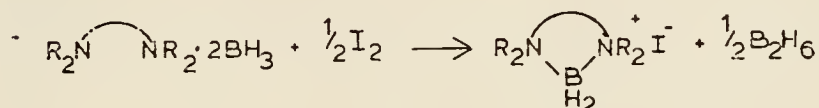
### SYNTHESIS OF CYCLIC BORONIUM CATIONS DERIVED FROM TERTIARY POLYAMINE-BORANES

#### Cyclic Cations Derived from Reactions of Polyamine-Boranes with Iodine or Trimethylamine-Iodoborane

A new, rapid and high yield synthesis of cyclic boronium cations is described in this chapter. Reaction of polyamine-boranes derived from tertiary polyamines, as described in the previous chapter, with iodine or trimethylamine-iodoborane under appropriate conditions, provides high yields of cyclic boronium cations. Iodine is the preferred reactant for all polyamines investigated, except those possessing sites which are reactive toward iodine or intermediates produced during the reaction.

General procedure of synthesis. The apparatus consists of a 250 ml Erlenmeyer flask, fitted with a straight vacuum distillation adapter, used for the passage of nitrogen into the flask, and a reflux condenser. An outlet tube leading to a bubbler containing a benzene-amine mixture is attached to the top of the condenser to trap diborane gas liberated from the reaction. The apparatus was suitable for reactions with either iodine or trimethylamine-iodoborane. In a typical reaction a stoichiometric amount of iodine or trimethylamine-iodoborane is allowed to react with a benzene

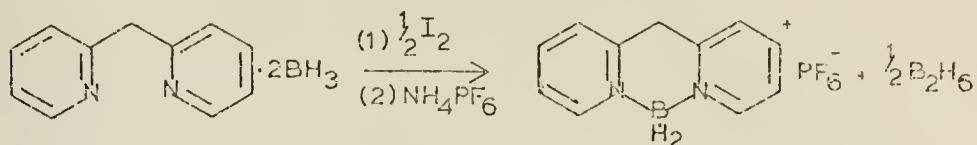
solution or slurry of the polyamine-borane, while being heated just below reflux. Nitrogen gas is continuously passed above the solution to remove diborane from the reaction. Reaction times varied from 1 to 24 hours, depending on the polyamine-borane employed. Ten hours, however, was sufficient in all but a few cases. All salts were converted to the more stable and more easily analyzed hexafluorophosphates. Quantities were calculated on the basis of the following equations:



Diborane generated in the above reactions can be recovered in high yields as polyamine-borane, suitable for further reaction, if sufficient care is extended to exclude all moisture and oxygen from the system, thus, conserving an expensive reactant.

The general procedure is exemplified in the synthesis of 2,2'-dipyridylmethanedihydroboron (1<sup>+</sup>) hexafluorophosphate, and will be referred to as the "general procedure" throughout this chapter.

Synthesis of 2,2'-dipyridylmethanedihydroboron (1<sup>+</sup>) hexafluorophosphate.



To a stirred slurry of 2,2'-dipyridylmethane-bis(borane) (1.00 g, 5.07 mmol) in dry benzene (100 ml) was added solid iodine (0.647 g, 2.55 mmol). An immediate reaction ensued with the evolution of hydrogen gas and a dark brown solution resulted. The flask was attached to a vacuum distillation adapter and a reflux condenser, to which a benzene-amine bubbler was attached. The reaction mixture was heated just below reflux in an oil bath. The solution became colorless and precipitation of a white solid ensued. The presence of diborane above the reaction was confirmed by its reaction with moist silver nitrate paper. Nitrogen gas was passed continuously through the system to remove the liberated diborane. The reaction appeared to be complete within 2 hours, as evidenced by the absence of any further diborane generation. An additional 3 hours of reaction time were employed to ensure complete reaction. Upon cooling, the white solid was removed by vacuum-filtration, washed with dry benzene (30 ml), diethyl ether (30 ml) and vacuum-dried (yield 1.561 g, 99.3%).

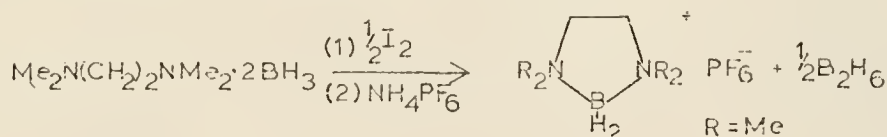
Conversion to the hexafluorophosphate salt was accomplished by dissolving the iodide salt (0.534 g, 1.72 mmol) in H<sub>2</sub>O

(20 ml), and adding 5M  $\text{NH}_4\text{PF}_6$  (2 ml). The mixture was cooled in an ice bath, vacuum-filtered, washed with ice cold water (30 ml), three portions (50 ml) of dry ether, and vacuum-dried (yield 0.531 g, 94.1%); mp  $196^\circ$ , dec. Anal. Calcd. for  $\text{C}_{11}\text{H}_{12}\text{BN}_2^+ \cdot \text{PF}_6^-$ : C, 40.24; H, 3.65; N, 8.54; B, 3.29. Found: C, 40.29; H, 3.71; N, 8.52; B, 3.12.

Proton nmr in  $\text{CH}_3\text{CN}$ : singlet at -4.86 ppm and three complex multiplets at -7.91 ppm, -8.33 ppm and -8.75 ppm, with an intensity ratio of 2:4:2:2, respectively. The  $^{11}\text{B}$  nmr in  $\text{CH}_3\text{CN}$ : triplet at 23.1 ppm from trimethylborate. The B-H coupling constant was approximately 110 Hz.

Infrared: doublet centered at  $2450\text{ cm}^{-1}$ , assigned to B-H stretching mode. Additional absorptions: 1640 (s), 1590 (w), 1500 (s), 1468, 1418, 1318, 1280 (w), 1222 (w), 1170 (w), 1138 (s), 1090, 840 (s, broad, structured, assigned to  $\text{PF}_6$ ),  $772\text{ cm}^{-1}$ .

Synthesis of N,N,N',N'-tetramethyl-1,2-ethanediamine-bis(dihydroboron ( $1^+$ ) hexafluorophosphate).

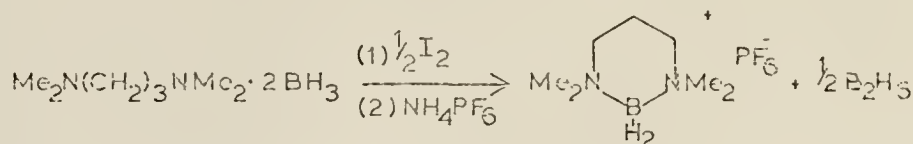


A sample of N,N,N',N'-tetramethyl-1,2-ethanediamine-bis(borane), (1.00 g, 5.94 mmol) was reacted with solid iodine (0.886 g, 3.49 mmol) in dry benzene, according to the general procedure. The reaction appeared to be complete within 1 hour. Heating was continued for an additional 3 hours to ensure complete reaction. A white solid (yield 1.69 g, 95.4%) was collected.

The iodide salt (0.748 g, 2.92 mmol) was converted to the hexafluorophosphate salt (yield 0.738 g, 92.3% recovery); mp 245°, dec. lit.<sup>25-27</sup> 240-244° dec. Anal. Calcd. for  $C_6H_{18}BN_2^+$ ,  $PF_6^-$ : C, 26.30; H, 6.57; N, 10.23. Found: C, 26.39; H, 6.78; N, 10.12.

The proton nmr and infrared spectra were identical to those previously reported.<sup>25-27</sup>

Synthesis of N,N,N',N'-tetramethyl-1,3-propanediamine dihydroboron (1+) hexafluorophosphate.



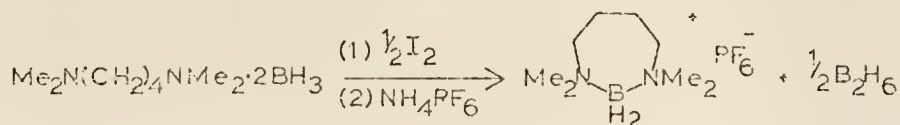
A sample of N,N,N',N'-tetramethyl-1,3-propanediamine-bis(borane) (1.00 g, 6.40 mmol) was reacted with solid iodine (0.816 g, 3.21 mmol) in dry benzene, according to the general procedure. After 8 hours of heating, only a small amount of solid was present and diborane was still being evolved. Heating was continued for an additional 18 hours to ensure complete reaction. A white solid (yield 1.64 g, 95.3%) was collected.

The iodide salt (1.04 g, 3.87 mmol) was converted to the hexafluorophosphate salt (yield 0.901 g, 81.3% recovery); mp 243°, dec. lit.<sup>26,27</sup> 241-245°, dec. Anal. Calcd. for  $C_7H_{20}BN_2^+$ ,  $PF_6^-$ : C, 29.19; H, 7.90; N, 9.73. Found: C, 29.39; H, 7.45; N, 9.61.

The proton nmr and infrared spectra were identical to those previously reported.<sup>26,27</sup>



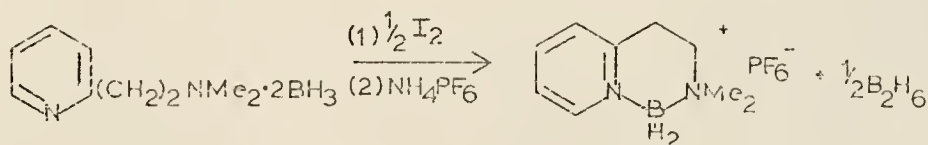
Synthesis of N,N,N',N'-tetramethyl-1,4-butanediamine-bis(hydroboron (1<sup>+</sup>) hexafluorophosphate).



A sample of N,N,N',N'-tetramethyl-1,4-butanediamine-bis(borane) (1.02 g, 5.93 mmol) was reacted with solid iodine (0.753 g, 2.96 mmol) in dry toluene, according to the general procedure. After 6 hours of heating, only a small amount of solid was present and diborane was still being evolved. Heating was continued for an additional 18 hours to ensure complete reaction. A white solid (yield 1.53 g, 90.8%) was collected. The iodide salt (0.988 g, 3.48 mmol) was converted to the hexafluorophosphate salt (yield 0.701 g, 66.7% recovery); mp 230°, dec. lit.<sup>26,27</sup> 230-231° dec. Anal. Calcd. for C<sub>8</sub>H<sub>22</sub>BN<sub>2</sub><sup>+</sup>, PF<sub>6</sub><sup>-</sup>: C, 31.81; H, 7.34; N, 9.28. Found: C, 31.78; H, 7.40; N, 9.23.

The proton nmr and infrared spectra were identical to those previously reported.<sup>26,27</sup>

Synthesis of 2-(2-dimethylaminoethyl) pyridine-bis(hydroboron (1<sup>+</sup>) hexafluorophosphate).



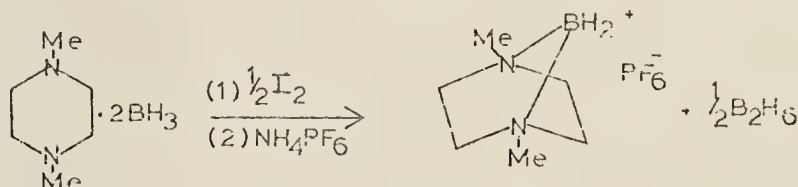
A sample of 2-(2-dimethylaminoethyl) pyridine-bis(borane) (1.00 g, 5.64 mmol) was reacted with solid iodine (0.716 g,

2.82 mmol), in dry benzene, according to the general procedure. The reaction appeared to be complete within 2 hours. Heating was continued for an additional 2 hours to ensure complete reaction. A white solid (yield 1.57 g, 96.3%) was collected.

The iodide salt (1.02 g, 3.51 mmol) was converted to the hexafluorophosphate salt (yield 1.00 g, 92.6% recovery); mp 132°, lit.<sup>26,27</sup> 132-133.5°. Anal. Calcd. for  $C_9H_{14}BN_2^+$ ,  $PF_6^-$ : C, 35.09; H, 5.24; N, 9.10. Found: C, 34.96; H, 5.10; N, 8.95.

The proton nmr and infrared spectra were identical to those previously reported.<sup>26,27</sup>

Synthesis of N,N'-dimethylpiperazinedihydroboron (1<sup>+</sup>) hexafluorophosphate.

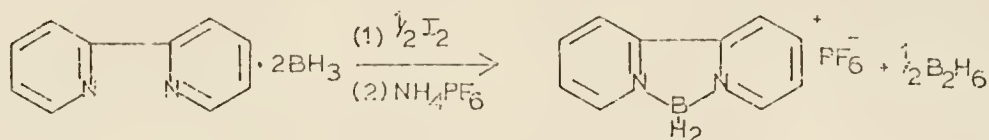


A sample of N,N'-dimethylpiperazine-bis(borane) (1.00 g, 7.04 mmol) was reacted with solid iodine (0.895 g, 3.52 mmol) in dry benzene, according to the general procedure. The reaction was heated for 15 hours to ensure complete reaction. A white solid (yield 1.68 g, 93.9%) was collected.

The iodide salt (1.01 g, 3.98 mmol) was converted to the hexafluorophosphate salt (yield 0.762 g, 70.8% recovery); mp 267°, lit.<sup>26</sup> 265-267°. Anal. Calcd. for  $C_{16}H_{16}BN_2^+$ ,  $PF_6^-$ : C, 26.49; H, 5.93; N, 10.29. Found: C, 26.47; H, 6.01; N, 10.20.

The proton nmr and infrared spectra were identical to those previously reported.<sup>26</sup>

Synthesis of 2,2'-bipyridyldihydroboron (1<sup>+</sup>) hexafluorophosphate.



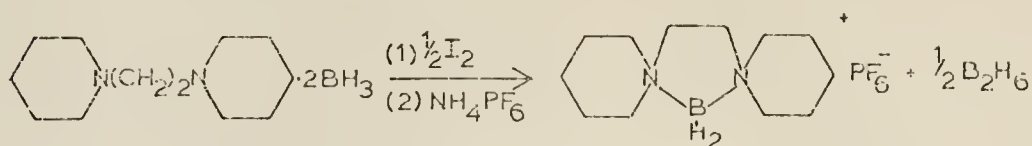
A sample of 2,2'-bipyridyl-bis(borane) (0.881 g, 4.79 mmol) was reacted with solid iodine (0.611 g, 2.41 mmol) in dry benzene, according to the general procedure. The reaction appeared to be complete within 1 hour, and no diborane was detectable above the solution after 1.5 hours of heating. A yellow solid (yield 1.20 g, 84.6%) was collected.

The iodide salt (1.18 g, 3.99 mmol) was converted to the hexafluorophosphate salt (yield 1.05 g, 84.0% recovery); mp 189°, dec. lit.<sup>25</sup> 170°, dec. Anal. Calcd. for  $\text{C}_{10}\text{H}_{10}\text{BN}_2^+ \text{PF}_6^-$ : C, 38.2; H, 3.18; N, 8.92. Found: C, 37.9; H, 3.24; N, 8.97.

Proton nmr in  $\text{CH}_3\text{CN}$ : three complex multiplets centered at -7.98 ppm, -8.53 ppm, and -8.83 ppm, with an intensity ratio of 2:4:2, respectively.

Infrared: doublet centered at  $2440 \text{ cm}^{-1}$ , assigned to the B-H stretching mode. Additional absorptions: 3100 (broad), 1680 (s), 1582 (s), 1516 (w), 1489 (s), 1470 (s), 1329 (s), 1171 (s), 1130 (s), 1100 (w), 1080 (s), 1050 (s), 840 (broad, structured, assigned to  $\text{PF}_6^-$ ),  $552 \text{ (s) cm}^{-1}$ .

Synthesis of 1,2-(N,N'-bis-piperidine) ethanedihydro-  
boron (1<sup>+</sup>) hexafluorophosphate.



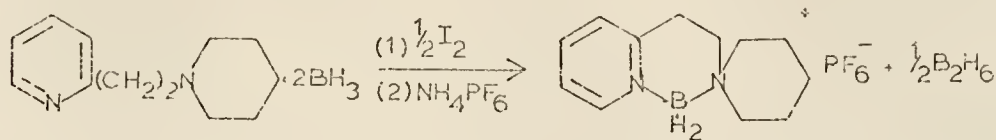
A sample of 1,2-(N,N'-bis-piperidine) ethane-bis(borane) (1.00 g, 4.69 mmol) was reacted with solid iodine (0.595 g, 2.34 mmol) in dry benzene, according to the general procedure. The reaction appeared to be complete within 2 hours, and no diborane was detectable above the solution after 3 hours of heating. A white solid (yield 1.42 g, 93.0%) was collected.

The iodide salt (0.981 g, 3.01 mmol) was converted to the hexafluorophosphate salt (yield 0.965 g, 93.2% recovery); mp 125°. Anal. Calcd. for  $\text{C}_{12}\text{H}_{26}\text{BN}_2^+ \text{PF}_6^-$ : C, 40.68; H, 7.34; N, 7.91. Found: C, 40.62; H, 7.44; N, 7.91.

Proton nmr in  $\text{CH}_2\text{Cl}_2$ : singlet at -3.41 ppm, and two complex multiplets centered at -1.73 ppm and -3.06 ppm, with an intensity ratio of 4:12:8, respectively.

Infrared: doublet centered at  $2470 \text{ cm}^{-1}$ , assigned to the B-H stretching mode. Additional absorptions: 2960 (s), 1480, 1455, 1340, 1320, 1300, 1255, 1190 (s), 1170, 1155 (s), 1095 (w), 1040 (s), 955, 930, 920, 845 (broad, structured, assigned to  $\text{PF}_6^-$ ), 778, 550 (s)  $\text{cm}^{-1}$ .

Synthesis of 2-(2-N-piperidinoethyl)-pyridinedihydro-boron (1<sup>+</sup>) hexafluorophosphate.



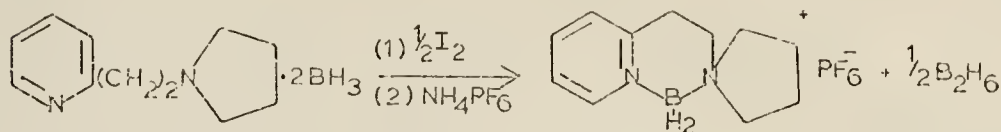
A sample of 2-(2-N-piperidinoethyl)-pyridine-bis(borane) (1.32 g, 6.03 mmol) was reacted with solid iodine (0.765 g, 3.01 mmol) in dry benzene, according to the general procedure. The reaction appeared to be complete within 1.5 hours, and no diborane was detectable above the solution after 2 hours of heating. A white solid (yield 1.80 g, 90.1%) was collected.

The iodide salt (1.50 g, 4.55 mmol) was converted to the hexafluorophosphate salt (yield 1.46 g, 92.4% recovery); mp 127°. Anal. Calcd. for  $\text{C}_{12}\text{H}_{20}\text{BN}_2^+ \text{PF}_6^-$ : C, 41.38; H, 5.75; N, 8.05. Found: C, 41.39; H, 5.75; N, 8.03.

Proton nmr in  $\text{CH}_2\text{Cl}_2$ : broad singlet with fine structure at -3.46 ppm, and four complex multiplets centered at -1.78 ppm, -3.03 ppm, -7.62 ppm and -8.21 ppm, with an intensity ratio of 4:6:2:2, respectively.

Infrared: strong absorption centered at  $2440 \text{ cm}^{-1}$ , assigned to the B-H stretching mode. Additional absorptions: 2960 (w), 2385 (w), 1632 (s), 1580, 1505, 1470, 1455 (s), 1435, 1390 (w), 1322, 1313, 1195 (s), 1150 (s), 1120, 1100 (s), 1060, 1040, 1000, 845 (broad, structured, assigned to  $\text{PF}_6^-$ ), 790, 770, 550 (s)  $\text{cm}^{-1}$ .

Synthesis of 2-(2-N-pyrrolidinoethyl)pyridine-dihydro-boron (1<sup>+</sup>) hexafluorophosphate.



A sample of 2-(2-N-pyrrolidinoethyl)pyridine-bis(borane) (1.27 g, 6.20 mmol) was reacted with solid iodine (0.788 g, 3.10 mmol) in dry benzene, according to the general procedure. The reaction appeared to be complete within 1.5 hours, and no diborane was detectable above the solution after 2 hours of heating. A white solid (1.76 g, 90.3%) was collected.

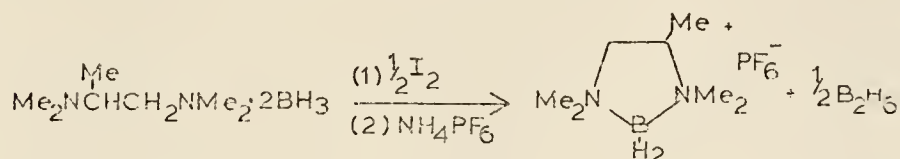
The iodide salt (1.50 g, 4.75 mmol) was converted to the hexafluorophosphate salt (yield 1.38 g, 87.8% recovery); mp 118°. Anal. Calcd. for  $\text{C}_{11}\text{H}_{18}\text{BN}_2^+\text{PF}_6^-$ : C, 39.52; H, 5.39; N, 8.38. Found: C, 39.49; H, 5.39; N, 8.36.

Proton nmr in  $\text{CH}_2\text{Cl}_2$ : broad singlet with fine structure at -3.49 ppm, and four complex multiplets centered at -2.15 ppm, -3.17 ppm, -7.67 ppm, and -8.17 ppm, with an intensity ratio of 4:4:4:2:2, respectively.

Infrared: strong absorption centered at  $2450\text{ cm}^{-1}$ , assigned to the B-H stretching mode. Additional absorptions: 2990 (w), 2385, 1632 (s), 1580, 1503 (s), 1470, 1459, 1440, 1400 (w), 1340 (w), 1305 (w), 1275, 1260, 1225, 1195, 1160 (s), 1125, 1095, 1020, 845 (broad, structured, assigned to  $\text{PF}_6^-$ ), 765 (s), 600 (s)  $\text{cm}^{-1}$ .



Synthesis of N,N,N',N'-tetramethyl-1,2-propanediamine-di-  
hydroboron (1<sup>+</sup>) hexafluorophosphate.



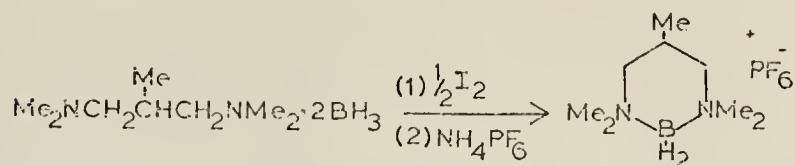
A sample of N,N,N',N'-tetramethyl-1,2-propanediamine-bis(borane) (1.00 g, 6.33 mmol) was reacted with solid iodine (0.805 g, 3.16 mmol) in dry benzene, according to the general procedure. The reaction appeared to be complete within 1.5 hours, and no diborane was detectable above the solution after 2 hours of heating. A white solid (yield 1.65 g, 96.2%) was collected.

The iodide salt (0.795 g, 2.94 mmol) was converted to the hexafluorophosphate salt (yield 0.780 g, 92.0% recovery); mp 161° dec. Anal. Calcd. for  $\text{C}_7\text{H}_{20}\text{BN}_2^+\text{PF}_6^-$ : C, 29.07; H, 6.92; N, 9.69. Found: C, 28.95; H, 6.92; N, 9.75.

Proton nmr in  $\text{CH}_2\text{Cl}_2$ : doublet centered at -1.34 ppm, four singlets centered at -2.66 ppm, -2.76 ppm, -2.88 ppm, and -3.48 ppm, and a complex multiplet centered at -3.51 ppm, with an intensity ratio of 3:3:3:6:1:2, respectively.



Synthesis of N,N,N',N'-2-pentamethyl-1,3-propanediamine-  
dihydroboron (1<sup>+</sup>) hexafluorophosphate.



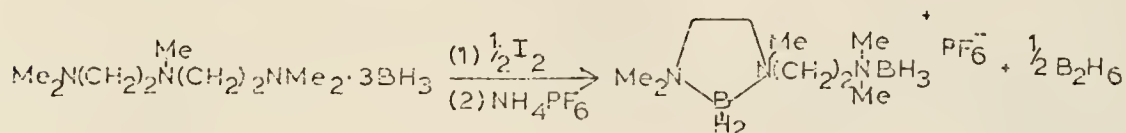
A sample of N,N,N',N'-2-pentamethyl-1,3-propanediamine-bis(borane) (1.00 g, 5.81 mmol) was reacted with solid iodine (0.739 g, 2.91 mmol) in dry benzene, according to the general procedure. After 2 hours of heating, only a small amount of solid was present in the reaction flask. The reaction was heated an additional 12 hours to ensure completion. A white solid (yield 1.55 g, 93.6%) was collected. The iodide salt (1.00 g, 3.51 mmol) was converted to the hexafluorophosphate salt (yield 0.934 g, 87.8% recovery); mp 164° dec. Anal. Calcd. for C<sub>8</sub>H<sub>21</sub>BN<sub>2</sub><sup>+</sup>PF<sub>6</sub><sup>-</sup>: C, 31.89; H, 6.98; N, 9.30. Found: C, 31.72; H, 7.34; N, 9.26.

Proton nmr in CD<sub>3</sub>CN: doublet centered at -0.95 ppm, two intense singlets centered at -2.66 ppm and -2.83 ppm, covering a complex multiplet centered at -2.68 ppm, with an intensity ratio of 3:6:6:5, respectively.

Infrared: doublet centered at 2460 cm<sup>-1</sup>, assigned to the B-H stretching mode. Additional absorptions: 2995, 2350, 1500 (s), 1480 (s), 1450 (s), 1420, 1400, 1390, 1345 (s), 1310, 1245 (s), 1215 (s), 1100 (s), 1125, 1105, 1080, 1055, 1115 (s), 995 (s), 965, 925 (s), 845 (broad,

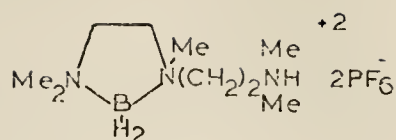
structured, assigned to  $\text{PF}_6^-$ ), 740, 600 ( $\text{s}$ )  $\text{cm}^{-1}$ .

Attempted synthesis of N,N,N',-trimethylethylenediamine-N' (2-trihydroborondimethylaminoethyl)dihydroboron ( $1^+$ ) hexafluorophosphate.



A sample of pentamethyldiethylenetriamine-tris(borane) (1.00 g, 4.63 mmol) was reacted with solid iodine (0.586 g, 2.31 mmol) in dry benzene, according to the general procedure. The reaction was heated for 8 hours to ensure completion. A white solid (yield 1.20 g, 78.8%) was collected.

The proton nmr in  $\text{D}_2\text{O}$  (gas evolution observed): singlet at -2.68 ppm, and two complex multiplets centered at -2.92 ppm and -3.60 ppm, with an intensity ratio of 2.96:12.5:7.5, respectively. The lack of correlation of the above spectrum suggested a mixture. Addition of solid  $\text{K}_2\text{CO}_3$  to the nmr tube caused considerable change in the spectrum. A new peak at -2.30 ppm, and a broad singlet with some fine structure at -2.95 ppm, appeared. Little change in the multiplet at -3.60 ppm was observed. Addition of a small amount of acid regenerated the initial spectrum. The above data supports the presence of ammonium salt in the mixture, believed to be the following:



When the reaction was carried out in  $\text{CH}_2\text{Cl}_2$ , rather than benzene, for a period of 30 hours, a material containing only a trace amount of the ammonium salt was obtained, as evidenced by the appearance of only a very small peak in the proton nmr of an alkaline  $\text{D}_2\text{O}$  solution.

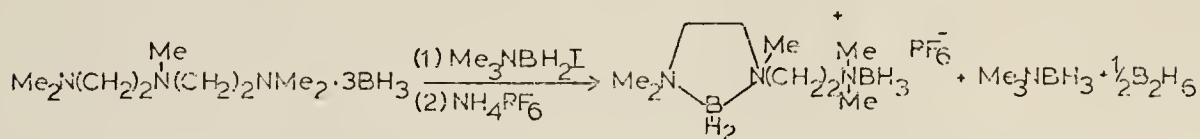
The iodide salt mixture (0.842 g), from the benzene procedure, was converted to the hexafluorophosphate salt. Gas evolution was observed during this conversion (yield 0.810 g, 91.3% recovery); mp  $149^\circ$ . Anal. Calcd. for  $\text{C}_9\text{H}_{28}\text{B}_2\text{N}_3^+$ ,  $\text{PF}_6^-$ : C, 31.30; H, 8.12; N, 12.17. Found: C, 30.32; H, 8.03; N, 12.35. Anal. Calcd. for  $\text{C}_9\text{H}_{25}\text{BN}_3^{+2}$ ,  $2\text{PF}_6^-$ : C, 22.64; H, 5.45; N, 8.81. The analytical data suggest a mixture. Attempts to recrystallize the material failed to improve the analytical data.

Proton nmr in  $\text{CD}_3\text{CN}$ : complex system of singlets centered at -2.60 ppm, -2.68 ppm, -2.85 ppm, -2.87 ppm, and -3.53 ppm, as well as, a very complex multiplet of a very low intensity, visible from -2.91 ppm to -3.67 ppm. The above spectrum did not correlate well with the expected, and provided further evidence of a mixture. However, if the small singlet at -2.68 ppm was assigned to the ammonium salt impurity, and combined with its borane derivative,

assigned at  $-2.60$  ppm, the resulting intensities of 6:3:6:4:4 correlate well with a mixture of the two described compounds. From integral ratios it was determined that the sample contained approximately 87% of the borane salt and 13% ammonium salt. The analytical data of a mixture of this composition correlates well with the analytical data obtained on the reaction product. Anal. Calcd. for mixture: C, 30.17; H, 7.77; N, 12.20. Found: C, 30.32; H, 8.03; N, 12.35.

A potential separation technique, based on solubility difference of the ( $1^+$ ) hexafluorophosphate salt, was developed on a microscale, employing proton nmr to confirm separation. A sample of the impure iodide salt was dissolved in  $D_2O$ . After gas evolution ceased, a small amount of solid  $K_2CO_3$  was added until the pH of the solution was increased to 10. A small amount of solid  $KPF_6$  was added, and the resulting white solid was removed by centrifuging the solution. The proton nmr of the remaining solution revealed two singlets centered at  $-2.26$  ppm and  $-3.58$  ppm, a broad, structured, intense peak at  $-2.88$  ppm, and a complex multiplet covering the area from  $-2.50$  ppm to  $-3.33$  ppm. The intensity ratio of 6:4:9:4, respectively, and chemical shifts were indicative of deprotonated ammonium salt impurity. There was no evidence of the borane derivative in the solution. No attempt was made to isolate this impurity.

Synthesis of N,N,N' trimethylethylenediamine-N' (2-trihydroboron dimethylaminoethyl)dihydroboron (1+) hexafluorophosphate, via trimethylamine-iodoborane.



Trimethylamine-borane (0.810 g, 11.1 mmol), in an Erlenmeyer flask (200 ml), was dissolved in dry toluene (75 ml). While continuously stirring the solution, solid iodine (1.40 g, 5.55 mmol) was added. After gas evolution had ceased, and the solution had become colorless, pentamethyldiethylenetriamine-tris(borane) (2.00 g, 9.30 mmol) was added. Reaction was continued according to the general procedure. The mixture was heated at 90° for 18 hours to ensure completion. A white solid (yield 2.95 g, 97%) was collected. The toluene solution, containing trimethylamine-borane, could be reused for additional reactions.

The proton nmr in alkaline D<sub>2</sub>O, revealed the absence of any ammonium salt. The iodide salt (1.79 g, 5.47 mmol) was converted to the hexafluorophosphate salt (yield 1.69 g, 89.5% recovery); mp 158-159°. Anal. Calcd. for C<sub>9</sub>H<sub>28</sub>B<sub>2</sub>N<sub>3</sub><sup>+</sup>, PF<sub>6</sub><sup>-</sup>: C, 31.30; H, 8.12; N, 12.17. Found: C, 31.34; H, 8.20; N, 12.17.

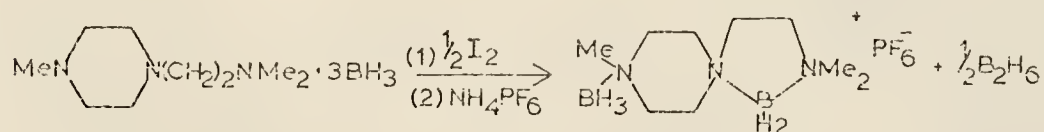
Proton nmr in CH<sub>3</sub>CN: four singlets centered at -2.60 ppm, -2.82 ppm, -2.86 ppm, and -3.51 ppm, and a complex multiplet of low intensity, covering the area from

-2.50 ppm to -3.33 ppm, with an intensity ratio of 6:3:6:4:4, respectively.  $^{11}\text{B}$  nmr in  $\text{CH}_3\text{CN}$ : quartet at 28.8 ppm and triplet at 13.7 ppm from trimethylborate. The B-H coupling constants were approximately 96 Hz and 108 Hz, respectively.

Infrared: complex absorption band covering the region from 2280 to 2518  $\text{cm}^{-1}$ , assigned to B-H stretching modes of both  $\text{BH}_2^+$  and  $\text{BH}_3$  entities. Additional absorptions: 1487 (s), 1470, 1465, 1460, 1445, 1325 (w), 1290 (w), 1252, 1220, 1205, 1173 (s), 1020 (s), 1000 (s), 960, 845 (broad, structured, assigned to  $\text{PF}_6^-$ ), 550 (s)  $\text{cm}^{-1}$ .

The presence of the  $\text{BH}_3$  functionality was confirmed by reaction of the iodide salt dissolved in  $\text{D}_2\text{O}$ , with iodine. The proton nmr was monitored for one hour, during which time the singlet assigned to the dimethylamino-borane group diminished in intensity, until it was totally absent from the spectrum. At the same time, a sharp new singlet appeared 19Hz downfield from the disappearing singlet, indicative of the formation of the ammonium ion. No attempt was made to isolate this material.

Synthesis of the cyclic boronium cation of N-methyl-N'-(2-dimethylaminoethyl)piperazine.





A sample of N-methyl-N'-(2-dimethylaminoethyl)piperazine-tris(borane) (2.00 g, 9.39 mmol) was reacted with solid iodine (1.19 g, 4.70 mmol) in dry benzene, according to the general procedure. The mixture was heated for 3 hours, at which time no diborane was detectable above the solution. A white solid (yield 2.75 g, 89.8%) was collected.

The proton nmr of the iodide salt in  $D_2O$ , with TMSF as an internal reference, revealed a complex spectrum consisting of two singlets centered at -2.80 ppm and -2.92 ppm, and two complex multiplets centered at -3.18 ppm and -3.66 ppm, with an intensity ratio of 3:6:4:8, respectively. It was observed that during the determination of this spectrum, a new peak centered at -2.53 ppm was appearing, suggesting hydrolysis of the  $BH_3$  group.

The iodide salt (1.01 g, 3.09 mmol) was converted to the hexafluorophosphate salt (yield 0.954 g, 98.7% recovery); mp 184-185°. Anal. Calcd. for  $C_9H_{26}B_2N_3^+$ ,  $PF_6^-$ : C, 31.48; H, 7.58; N, 12.24. Found: C, 31.29; H, 7.59; N, 12.16.

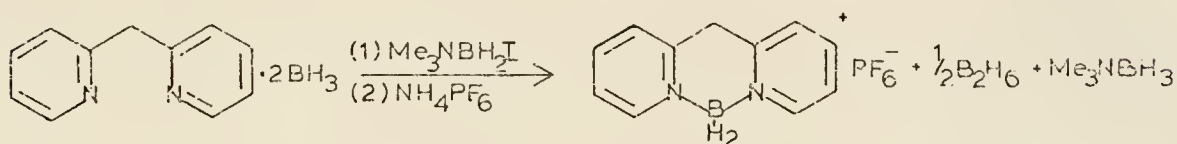
Proton nmr in  $CD_3Cl$ : complex spectrum consisting of two singlets centered at -2.63 ppm and -2.85 ppm, and two complex multiplets centered at -3.08 ppm and -3.52 ppm, with an intensity ratio of 3:6:4:8, respectively.

Infrared: complex absorption band covering the region from 2300 to 2520  $cm^{-1}$ , assigned to B-H stretching modes of both  $BH_2^+$  and  $BH_3$  entities. Additional absorptions:



1475 (broad, structured), 1360, 1350, 1315, 1260 (w), 1210 (s), 1165 (s), 1145, 1110, 1040 (w), 1010, 995, 978 (w), 950 (broad, structured), 845 (broad, structured, assigned to  $\text{PF}_6^-$ ), 550 (s)  $\text{cm}^{-1}$ .

Synthesis of 2,2'-dipyridylmethanedihydroboron ( $1^+$ ) hexafluorophosphate, via trimethylamine-iodoborane.

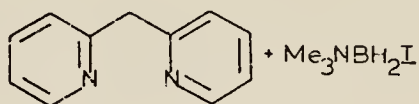


Trimethylamine-borane (1.01 g, 13.8 mmol), in an Erlenmeyer flask, was dissolved in dry benzene (75 ml). While continuously stirring the solution, solid iodine (1.75 g, 6.89 mmol) was added. After gas evolution had ceased, and the solution had become colorless, 2,2'-dipyridylmethane-bis(borane) (2.70 g, 13.8 mmol) was added. The reaction mixture was heated just below reflux for 18 hours, and diborane was removed under nitrogen. A white solid (yield 3.55 g, 83.0%) was collected.

The iodide salt (1.50 g, 4.84 mmol) was converted to the hexafluorophosphate salt (yield 1.45 g, 91.4%); mp  $196^\circ$ , dec..

The proton nmr and infrared spectra were identical to those of an authentic sample.

Reaction of 2,2'-dipyridylmethane with trimethylamine-iodoborane.



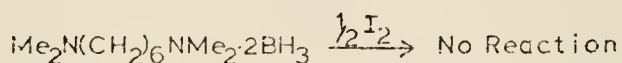
To a solution of trimethylamine-iodoborane, prepared by adding iodine (1.49 g, 5.87 mmol) to trimethylamine-borane (0.859 g, 11.8 mmol) dissolved in dry benzene (80 ml), was added 2,2'-dipyridylmethane (2.00 g, 11.8 mmol), with continuous stirring. The solution turned red-orange in color almost immediately.

The solution was refluxed for 80 hours, during which time a stream of nitrogen gas was passed above the reaction solution to remove liberated trimethylamine. The presence of trimethylamine was indicated by its reaction with moist litmus paper. The resulting orange solid was removed by vacuum-filtration, and vacuum-dried (yield 3.40 g, 92.9%).

Proton nmr in  $\text{CH}_2\text{Cl}_2$ : mixture of materials, as evidenced by three singlets at -2.66 ppm, -2.80 ppm, and -3.00 ppm, assigned to non-coupling methyl groups.

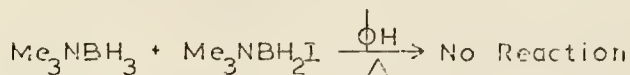
All attempts to isolate a pure, boron-containing material were unsuccessful. It is postulated that two of the materials present are the anhydro base of 2,2'-dipyridylmethane dihydro-boron cation, which gives rise to the intense red-orange color, and the ammonium salt of trimethylamine.

Attempted reaction of N,N,N',N'-tetramethylhexanediamine-bis(borane) with iodine.



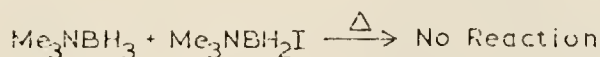
A sample of N,N,N',N'-tetramethylhexanediamine-bis(borane) (2.02 g, 10.1 mmol) was reacted with solid iodine (1.28 g, 5.03 mmol) in dry mesitylene, according to the general procedure. The mixture was refluxed for 4 weeks without production of any cationic material.

Attempted reaction of trimethylamine-borane with trimethylamine-iodoborane in benzene.



To a sample of trimethylamine-iodoborane (1.00 g, 5.03 mmol) in dry benzene (50 ml), prepared by the reaction of trimethylamine-borane (0.367 g, 5.03 mmol) and iodine (0.638 g, 2.51 mmol), was added trimethylamine-borane (0.367 g, 5.03 mmol). The mixture was refluxed for 30 hours with no visible evidence of diborane evolution, or reaction. The proton nmr of the solution revealed only the presence of starting materials.

Attempted reaction of trimethylamine-borane with trimethylamine-iodoborane neat.

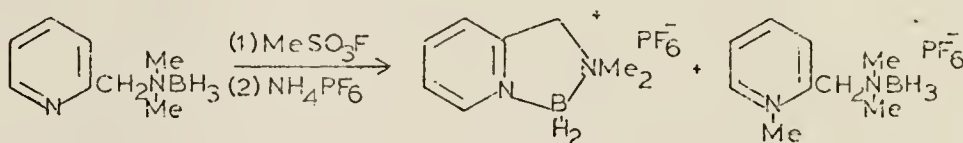


To a sample of trimethylamine-iodoborane (1.00 g, 5.03 mmol)

in a reaction flask (50 ml), prepared by the reaction described previously, was added trimethylamine-borane (0.367 g, 5.03 mmol). The reaction flask was connected to a vacuum line, purged, and sealed. The mixture was heated as a melt in an oil bath for 3 hours, cooled, and opened to the vacuum line. No gaseous material was observed. The proton nmr in  $\text{CH}_2\text{Cl}_2$  revealed only unchanged starting materials.

Synthesis of Cyclic Boronium Cations by Methods other than Reactions of Polyamine-Boranes with Iodine or Trimethylamine-Iodoborane

Synthesis of 2(-trihydroborondimethylaminomethyl)-N-methyl pyridinium (1+) hexafluorophosphate.



To a sample of 2(-trihydroborondimethylaminomethyl)pyridine, (1.00 g, 6.66 mmol), in an Erlenmeyer flask (125 ml), was added dry benzene (70 ml). While continuously stirring the solution, methyl fluorosulfonate (0.759 g, 6.66 mmol) was added. The solution was allowed to stir for 8 hours to ensure complete reaction. A white solid (yield 1.58 g, 89.8%) was filtered from the solution, washed with two portions (50 ml) of diethyl ether, and vacuum-dried.

Conversion to the hexafluorophosphate salt was accomplished by dissolving the fluorosulfonate salt

(1.58 g, 5.98 mmol) in  $\text{H}_2\text{O}$  (20 ml), and adding 5M  $\text{NH}_4\text{PF}_6$  (2 ml). The mixture was cooled in an ice bath, vacuum-filtered, washed with ice cold water (30 ml), three portions (50 ml) of dry ether, and vacuum-dried (yield 1.80 g, 97.1% recovery).

Proton nmr in  $\text{CD}_3\text{CN}$ : five singlets, and a large complex multiplet extending from -7.75 ppm to -9.10 ppm. The lack of correlation of this spectrum to that expected, suggested a mixture, thought to be that of the desired compound, and approximately 20% of the cyclic boronium cation. Separation was accomplished by washing the salt with three portions (15 ml) of  $\text{CH}_2\text{Cl}_2$ , which removed what was latter identified to be the cyclic boronium cation.

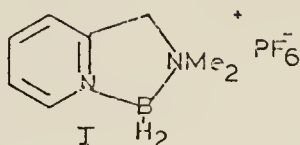
Proton nmr of the remaining solid (1.40 g, 75.5% overall yield) in  $\text{CD}_3\text{CN}$ : three singlets centered at -2.76 ppm, -4.38 ppm, and -4.58 ppm, and three complex multiplets centered at -8.08 ppm, -8.48 ppm, and -8.75 ppm, with an intensity ratio of 6:2:3:2:1:1, respectively.

Infrared: strong absorption, centered at  $2390\text{ cm}^{-1}$  assigned to B-H stretching mode. Additional absorptions: 3100, 3125, 3080, 1640 (s), 1595 (s), 1529, 1490, 1472 (s), 1452, 1420, 1385, 1350, 1315, 1280, 1242, 1210, 1175 (s), 1160 (s), 1025 (s), 1010 (s), 955 (s), 845 (broad, structured, assigned to  $\text{PF}_6^-$ ), 550 (s)  $\text{cm}^{-1}$ .

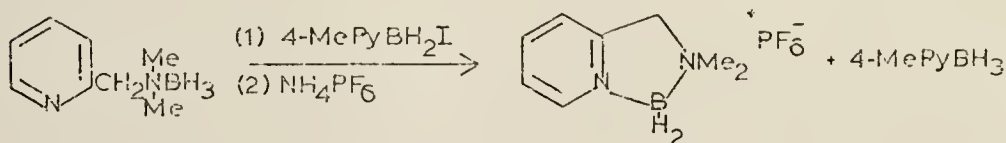
The above data correlates well with the expected product. Anal. Calcd. for  $\text{C}_9\text{H}_{18}\text{BN}_2^+\text{PF}_6^-$ : C, 34.84;

H, 5.81; N, 9.03. Found: C, 34.96; H, 5.79; N, 9.03;  
mp 120°.

The proton nmr spectrum of the  $\text{CH}_2\text{Cl}_2$  soluble impurity was found to be identical to that of the cyclic boronium cation (I).



Synthesis of 2(-dimethylaminomethyl)pyridinedihydro-  
boron (1<sup>+</sup>) hexafluorophosphate, via 4-methylpyridine-  
iodoborane.



A sample of 4-methylpyridine-borane (0.357 g, 3.33 mmol), in an Erlenmeyer flask (125 ml), was dissolved in dry  $\text{CH}_2\text{Cl}_2$  (30 ml). While continuously stirring the solution, solid iodine (0.421 g, 1.66 mmol) was added. After the iodine color was discharged, and no further gas evolution was observed, 2(-trihydroborondimethylaminomethyl)pyridine (0.500 g, 3.33 mmol) was added. The solution was stirred constantly for 3 hours, during which time diborane was observed above the solution. Dry diethyl ether (100 ml) was added to the reaction flask. A white solid precipitated, and was removed by filtration, washed with two portions (50 ml) of dry diethyl ether, and vacuum-dried (yield 0.810 g, 84.9% yield).







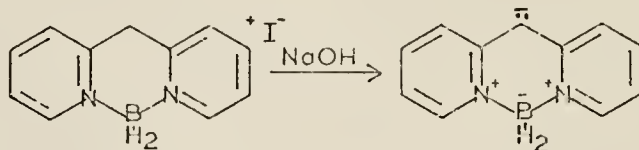
dried (yield 1.14 g, 73.5%); mp 122-123°. Anal. Calcd. for  $C_8H_{14}BN_2^+PF_6^-$ : C, 32.65; H, 4.76; N, 9.52. Found: C, 32.67; H, 4.80; N, 9.51.

Proton nmr in  $CH_2Cl_2$ : two singlets centered at -2.96 ppm and -4.71 ppm, and three complex multiplets centered at -7.83 ppm, -8.30 ppm, and -8.50 ppm, with an intensity ratio of 6:2:2:1:1, respectively.

Infrared: doublet centered at  $2474\text{ cm}^{-1}$ , assigned to B-H stretching mode. Additional absorptions: 2391 (s), 1640 (s), 1500 (s), 1485, 1470 (s), 1420, 1390, 1365, 1307 (s), 1280, 1250, 1207 (s), 1170, 1152, 1132, 1120, 1110, 1090 (s), 1030, 1000 (s), 970, 910 (s), 845 (broad, structured, assigned to  $PF_6^-$ ), 780, 760, 710, and  $550\text{ cm}^{-1}$ .

#### Reactions and Derivatives of 2,2'-Dipyridylmethanedihydroboron (1+) Salts

Synthesis of the anhydro base of 2,2'-dipyridylmethane-  
dihydroboron (1+) iodide.



A sample of 2,2'-dipyridylmethanedihydroboron (1+) iodide, (2.00 g, 6.48 mmol) was dissolved in water (28 ml). The solution was cooled in an ice bath while being stirred continuously. To this cooled solution was added 2N NaOH (6 ml), which produced a deep red-orange solution initially, and finally an orange precipitate.

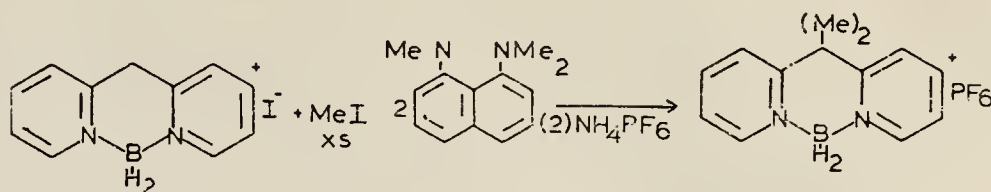
The precipitate was removed by vacuum-filtration, washed with cold water (20 ml), and vacuum-dried (yield 1.08 g, 91.6%); mp 83-84°. Anal. Calcd. for  $C_{11}H_{11}N_2B$ : C, 72.52; H, 6.04; N, 15.39. Found: C, 72.47; H, 6.10; N, 15.37; B, 6.06. The material was hygroscopic and appeared to be unstable on prolonged exposure to air. For these reasons, the sample was stored under vacuum in a dry box.

A sample of the orange solid was placed in a vacuum sublimator, and heated in an oil bath at 70°C, under a pressure of  $10^{-3}$  torr. The rate of sublimation was very slow and did not afford a reasonable means of recovery, due to decomposition under prolonged heating.

Proton nmr in  $CCl_4$ : sharp singlet centered at -4.93 ppm, and three complex multiplets centered at -6.28 ppm, -6.97 ppm, and -7.30 ppm, with an intensity ratio of 1:4:2:2, respectively.  $^{11}B$  nmr in  $CH_2Cl_2$ : triplet centered at 22.9 ppm from trimethylborate. The B-H coupling constant was approximately 100 Hz.

Infrared: strong absorption, centered at  $2450\text{ cm}^{-1}$ , assigned to B-H stretching mode. Additional absorptions: 2280, 2222, 1625 (s), 1560 (s), 1550, 1482 (s), 1463 (s), 1395, 1335, 1285 (w), 1190 (s), 1182, 1121, 1105, 1060, 1049, 1030, 991, 980, 979, 972, 955, 905, 878, 770 (s), 750, 721, 715,  $598\text{ cm}^{-1}$ .

Synthesis of 2,2-(2,2'-dipyridyldihydroboron)propane  
(1+) hexafluorophosphate.

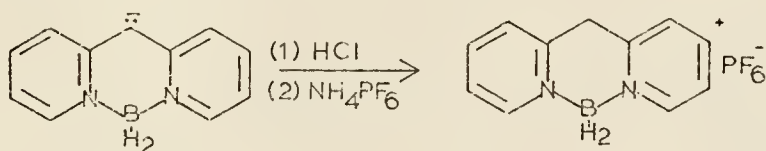


A sample of 2,2'-dipyridylmethanedihydroboron (1+) iodide (1.00 g, 3.23 mmol), in an Erlenmeyer flask (50 ml), was reacted with methyl iodide (10 ml), and bis-1,8-dimethylaminonaphthalene (1.40 g, 6.54 mmol). The orange-red solution was stirred continuously for 20 hours. The resulting solid was removed by vacuum-filtration, and washed with diethyl ether (50 ml). This solid was suspended in H<sub>2</sub>O, and the pH increased to approximately 8 with K<sub>2</sub>CO<sub>3</sub>. The remaining insoluble material (bis-1,8-dimethylaminonaphthalene ammonium (1+) iodide) was removed by filtration. The pH of the remaining aqueous solution was increased to approximately 10, giving rise to an orange color, and extracted with two portions (50 ml) of CH<sub>2</sub>Cl<sub>2</sub>. The pH of the solution was decreased to approximately 4 by the addition of 2N HCl, and 5M NH<sub>4</sub>PF<sub>6</sub> (2 ml) was added. The solution was cooled in an ice bath, and the white solid removed by filtration, washed with ice cold water (20 ml), diethyl ether (50 ml), and vacuum-dried (yield 0.987 g, 85.8%); mp 237°. Anal. Calcd. for C<sub>13</sub>H<sub>16</sub>BN<sub>2</sub><sup>+</sup>PF<sub>6</sub><sup>-</sup>: C, 43.82; H, 4.49; N, 7.87. Found: C, 43.76; H, 4.54; N, 7.92.

Proton nmr in DMSO- $D_6$ : sharp singlet at -1.93 ppm and three complex multiplets centered at -7.99 ppm, -8.50 ppm, -8.97 ppm, with an intensity ratio of 6:2:4:2, respectively.

Infrared: strong absorption centered at  $2460\text{ cm}^{-1}$ , assigned to B-H stretching mode. Additional absorptions: 1625 (s), 1590 (s), 1495 (s), 1453, 1405, 1375, 1319, 1270, 1170 (s), 1100, 1060, 1005, 845 (broad, structured, assigned to  $\text{PF}_6^-$ ), 780 (s), 550 (s)  $\text{cm}^{-1}$ .

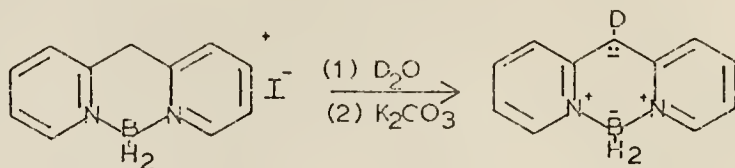
Protonation of the anhydro base derived from 2,2'-dipyridylmethanedihydroboron cation.



To a sample of the anhydro base of 2,2'-dipyridylmethanedihydroboron cation (0.244 g, 1.34 mmol), suspended in water (30 ml), was added 2N HCl, until a pH of approximately 2 was obtained. To the pale green solution was added 5M  $\text{NH}_4\text{PF}_6$  (4 ml). The resulting white solid was removed by filtration, washed with diethyl ether, and vacuum-dried (yield 0.380 g, 86.5%); mp  $194^\circ$ .

The proton nmr and infrared spectra were identical to those of an authentic sample.

Synthesis of the deuterated anhydro base of 2,2'-  
-dipyridylmethanedihydroboron ( $1^+$ ) iodide.

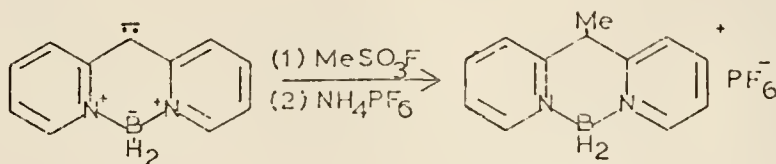


A sample of 2,2'-dipyridylmethanedihydroboron ( $1^+$ ) iodide (1.00 g, 3.23 mmol), in an Erlenmeyer flask (50 ml), was dissolved in  $D_2O$  (99%, 20 ml). The pH of the solution was adjusted to approximately 8 with  $K_2CO_3$ . The solution was stirred for 30 minutes, at which time the pH was increased to 10 with additional  $K_2CO_3$ . The resulting orange solid was removed by filtration, washed with ice cold  $D_2O$  (5 ml), and vacuum-dried (yield 0.550 g, 93.6%).

The proton nmr in  $CCl_4$  was identical to that of an authentic sample, except for considerable reduction of the singlet at -4.93 ppm, assigned to the lone methylene proton, which has undergone an exchange reaction with  $D_2O$ . From the relative intensities, the sample appeared to be approximately 85% deuterated.

The infrared spectrum revealed an increase in intensities of the following absorptions: 1060, 979, 972, 955, and a new peak at  $520\text{ cm}^{-1}$ .

Attempted synthesis of 1,1-(2,2'-dipyridyldihydroboron)ethane ( $1^+$ ) hexafluorophosphate.



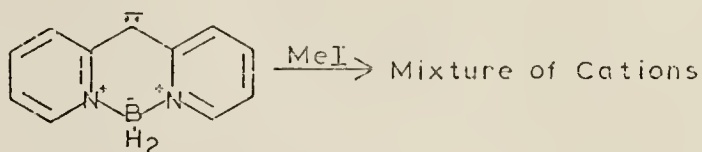
A sample of the anhydro base of 2,2'-dipyridylmethanedihydroboron cation (0.650 g, 3.57 mmol), in an Erlenmeyer flask (50 ml), was dissolved in  $\text{CH}_2\text{Cl}_2$  (30 ml), in a dry box. To this continuously stirred solution was added methyl fluorosulfonate (1.40 g, 12.3 mmol). After approximately 10 minutes, the initial orange solution had become a pale yellow. The volatiles were removed under vacuum, and water (30 ml) was added to the remaining yellow solid. The aqueous solution was filtered, and 5M  $\text{NH}_4\text{PF}_6$  (3 ml) was added. The resulting pale yellow solid was washed with ice cold water (20 ml), and vacuum-dried (yield 1.10 g, 89.8% recovery).

Proton nmr in  $\text{CH}_2\text{Cl}_2$ : doublet at -1.95 ppm ( $J_{\text{C-H}}$ , 7Hz), two small singlets at -1.97 ppm and -4.72 ppm, and three complex multiplets centered at -7.85 ppm, -8.35 ppm, and -8.69 ppm. The spectrum clearly indicated the presence of a mixture consisting of the monomethyl, dimethyl, and unsubstituted cations. From the integral ratios, the percent composition was approximately 94%, 3%, and 3%, respectively.



Separation of the dimethyl cation was accomplished by suspending the mixture in ice cold water (20 ml), and adjusting the pH to approximately 10. After approximately 10 minutes of stirring, the red-orange precipitate was removed by vacuum-filtration, washed with ice cold water (20 ml), redissolved in 0.1N HCl (10 ml), and precipitated as the hexafluorophosphate salt by the addition of 5M  $\text{NH}_4\text{PF}_6$  (2 ml). The resulting white solid was washed with ice cold water (10 ml), and vacuum-dried. The proton nmr in  $\text{CH}_2\text{Cl}_2$ , revealed a mixture containing only the monoethyl and unsubstituted cations. No further attempts were made to separate these cations.

Reaction of the anhydro base of 2,2'-dipyridylmethanedi-hydroboron cation with methyl iodide.



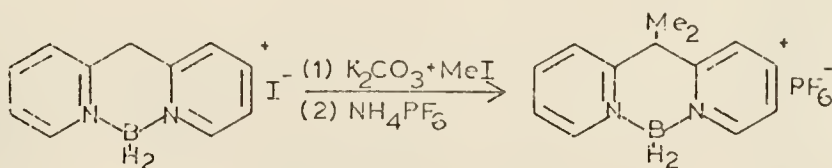
A sample of the anhydro base of 2,2'-dipyridylmethanedi-hydroboron cation (0.432 g, 2.37 mmol), in an Erlenmeyer flask (50 ml), was dissolved in  $\text{CH}_3\text{I}$  (30 ml). The deep red-orange solution was stirred continuously until the color was discharged, approximately 72 hours. The volatiles were removed under vacuum, and the remaining solid was dissolved in  $\text{CH}_2\text{Cl}_2$ , filtered, precipitated with hexane, filtered, and vacuum-dried (yield 0.728 g, 94.8%).



Conversion to the hexafluorophosphate salt was accomplished by dissolving the iodide salt in water (25 ml), and adding 5M  $\text{NH}_4\text{PF}_6$  (3 ml). The solution was cooled in an ice bath, filtered, washed with ice cold water (20 ml), and vacuum-dried (yield 0.690 g, 85.1% recovery).

The proton nmr in  $\text{CH}_2\text{Cl}_2$  revealed a mixture containing the monomethyl, dimethyl, and unsubstituted cations. From the integral ratios, the mixture was determined to be approximately 80% monomethyl cation, 10% dimethyl cation, and 10% unsubstituted cation. Separation from the dimethyl cation was achieved by the addition of base, filtration of the insoluble anhydro bases of the monomethyl and unsubstituted cations, acidification of these anhydro bases, and conversion to their hexafluorophosphate salts. Attempts to separate the monomethyl and unsubstituted cations from one another were unsuccessful.

Reaction of 2,2'-dipyridylmethanedihydroboron ( $1^+$ ) iodide, with methyl iodide, and potassium carbonate.

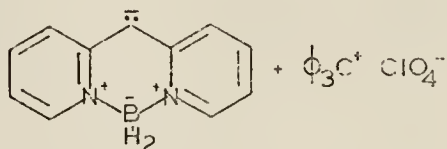


To a sample of 2,2'-dipyridylmethanedihydroboron ( $1^+$ ) iodide (0.502 g, 1.62 mmol), in an Erlenmeyer flask (50 ml), was added  $\text{CH}_3\text{CN}$  (30 ml),  $\text{CH}_3\text{I}$  (5 ml), and anhydrous  $\text{K}_2\text{CO}_3$  (0.566 g, 4.07 mmol). The red-orange mixture was heated at  $40^\circ$  for 18 hours, with continuous

stirring. The volatiles were removed under vacuum, and the resulting solid was acidified with 1N HCl until all gas evolution had ceased. The addition of 5M  $\text{NH}_4\text{PF}_6$  (3 ml) produced a white solid which was removed by vacuum-filtration and vacuum-dried (yield 0.501 g, 86.8% recovery).

The proton nmr in  $\text{CH}_2\text{Cl}_2$  revealed a mixture of the monosubstituted, disubstituted, and unsubstituted cations. The predominant material was that of the disubstituted cation. No attempts were made to separate the mixture. However, employment of long reaction times should provide a pure product.

Reaction of the anhydro base of 2,2'-dipyridylmethanedi-hydroboron cation with tritylperchlorate.



A sample of the anhydro base of 2,2'-dipyridylmethanedi-hydroboron cation (0.500 g, 2.75 mmol), in an Erlenmeyer flask (50 ml), was dissolved in dry benzene (30 ml) in a dry box. To this solution was added freshly prepared, dry tritylperchlorate (0.943 g, 2.75 mmol). The red-orange solution lightened and it appeared as if a new solid was formed. The solution was stirred for 14 hours and filtered. The red-orange solid was washed with dry benzene (10 ml), and vacuum-dried (yield 0.983 g, 129% of theoretical).

The combined benzene solutions were evaporated to dryness, and a solid material (0.685 g) was recovered. The proton nmr of this material confirmed its identity as tritylmethane (yield 102%).

Several attempts to isolate and characterize other reaction products were unsuccessful, and the lack of solubility of reaction products in solvents that would not react, made purification virtually impossible. The isolation and identification of tritylmethane does provide evidence that hydride abstraction did occur, and that a new boron-containing material does exist.

The yields of both the iodide salts, hexafluorophosphate salts, overall yields of hexafluorophosphate salts, anhydro bases, and melting points of all compounds contained in this chapter appear in Table III.

Table III

Yields and Melting Points of Cations and Derivatives

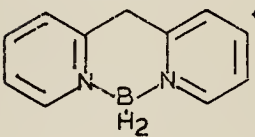
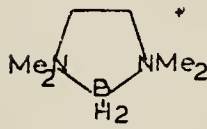
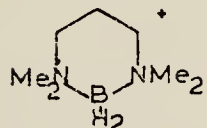
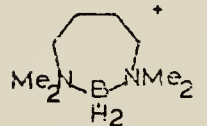
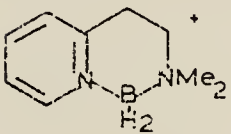
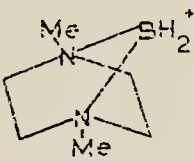
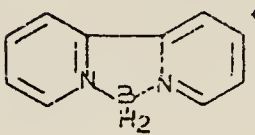
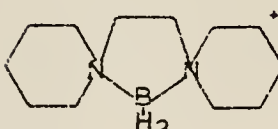
Compound	Yield %	I <sup>-</sup>	PF <sub>6</sub> <sup>-</sup> <sup>a</sup>	PF <sub>6</sub> <sup>-</sup> <sup>b</sup>	Mp °C	Lit
	99.3	94.1	93.4	196	---	
	95.4	92.3	88.1	245	240-244 <sup>c,d</sup>	
	95.3	81.3	77.5	243	241-245 <sup>d,e</sup>	
	90.8	66.7	60.6	230	230-231 <sup>d,e</sup>	
	96.3	92.6	89.2	132	132-133 <sup>d,e</sup>	
	93.9	70.8	66.5	267	265-267 <sup>e</sup>	
	84.6	84.0	77.1	189	170 <sup>c</sup>	
	93.1	93.2	86.7	125	---	

Table III(continued)

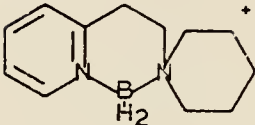
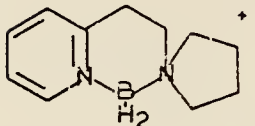
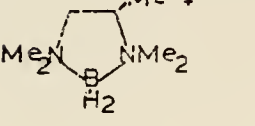
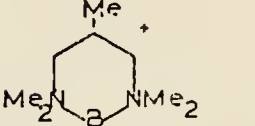
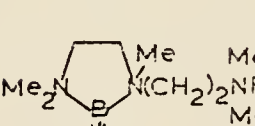
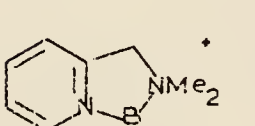
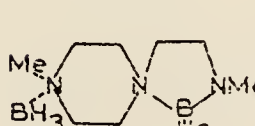
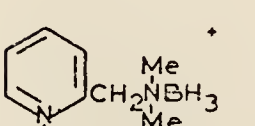
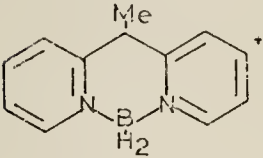
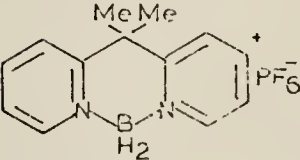
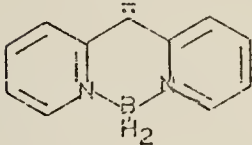
Compound	Yields %	I <sup>-</sup>	PF <sub>6</sub> <sup>-a</sup>	PF <sub>6</sub> <sup>-b</sup>	Mp <sup>o</sup> C	Lit
	90.1	92.4	88.3	127	---	
	90.3	87.8	72.3	118	---	
	96.2	92.0	88.5	161	---	
	93.6	87.8	82.2	164	---	
	97.0	89.5	86.8	158-159	---	
	84.9	95.0	80.7	122-123	---	
	69.8	98.7	88.6	184-185	---	
	---	---	75.5	120	---	

Table III (continued)

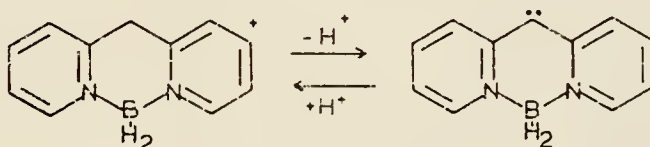
Compound	Yield %	I <sup>-</sup>	PF <sub>6</sub> <sup>-</sup> <sup>a</sup>	PF <sub>6</sub> <sup>-</sup> <sup>b</sup>	Mp °C	Lit
			mixture of products			-----
	-----	-----	-----	85.8	237	-----
	91.6	-----	-----	-----	83-84	-----

<sup>a</sup>Percent recovered from iodide salt; <sup>b</sup> Overall yield;  
<sup>c</sup> N. E. Miller and E. L. Muetterties, *J. Am. Chem. Soc.*,  
86, 1033(1964); <sup>d</sup> T. E. Sullivan, Doctoral Dissertation,  
University of Florida, (1970); <sup>e</sup> G. E. Ryschkewitsch and  
T. E. Sullivan, *Inorg. Chem.*, 9, 899(1970);

CHAPTER VI  
PHYSICAL MEASUREMENTS

Acid-Base Dissociation Constant Determination Using  
Electronic Spectra

The reactions of the red-orange, aqueous solution of the anhydro base of the cyclic boronium cation derived from 2,2'-dipyridylmethane, with acid, produced a colorless solution, suggesting the use of a colorimetric method to determine the acid dissociation constant.



The spectra for each compound was obtained with a Beckman DB recording spectrophotometer, using 1cm square, fused-silica cells. The equilibrium was shifted to both extremes with 0.10M HCl to observe the protonated compound, and with 0.10M NaOH to observe the unprotonated compound. It was found that the protonated compound failed to show any absorption in the 600-300 (nm) region, while the deprotonated compound revealed several absorptions in this region (see fig. I), and it was possible, by carefully monitoring the pH of the solution, to determine the  $K_a$  of the acid-base conjugate pairs.

Employing the method described by Deutsch and Taube,<sup>31</sup>



and by assuming that as the pH is lowered the unprotonated form is converted to the protonated form, the following relationship applies.

$$K_a = \frac{[H^+](E\lambda^{OBS} - E\lambda^H)}{(E\lambda^{OBS} - E\lambda^{NEUT})}$$

Where  $[H^+]$  is the hydronium ion concentration,  $E\lambda^{OBS}$  is the extinction coefficient observed at wavelength  $\lambda$  of the intermediate pH solutions,  $E\lambda^H$  is the extinction coefficient observed at wavelength  $\lambda$  of the completely protonated form, and  $E\lambda^{NEUT}$  is the extinction coefficient observed at wavelength  $\lambda$  of the completely unprotonated form. The pH of the intermediate solutions was kept constant by employing suitable buffers, and care was taken to choose a wavelength to monitor that was not affected by the absorptions of the buffers.<sup>32</sup> Only those pH's where the transmittance fell in the middle 60% range of the total difference between the completely protonated and completely unprotonated forms were used in the calculations of the  $K_a$ , and the pH of the buffered solutions was checked with a Corning 12 Research pH meter, using the expanded scale. In this study it was imperative that all solutions be oxygen-free, due to what appeared to be a decomposition of the material in alkaline solution when oxygen was present.

By taking the spectrum at every pH unit from 7 to 12, the pH range was found where significant quantities of both acid and base are in equilibrium. The spectra of those solutions whose pH varied approximately 0.13 of a pH unit within this range were taken against a buffer solution reference, and extinction coefficients were calculated. From the extinction coefficients and the pH of the solutions, the  $K_a$  was obtained. The total concentration of the absorbing species, wavelength monitored, data obtained, and calculated  $K_a$ 's, are listed in Table IV.

#### Infrared Spectra

The infrared spectra were obtained from KBr pellets, using the Beckman IR-10, or the Perkin-Elmer 137 instrument. The detailed infrared data of all compounds not previously reported, were included with their synthesis in Chapters III-V.

Infrared was used in this study only as a tool to characterize the presence of certain functional groups (i.e.,  $BH_2^+$ ,  $BH_3$ , OH), and detailed analyses of the spectra were not performed. In the case of the polyamine-boranes, and boron cations, the spectra are similar to those reported in the literature.<sup>25,30,33,34</sup> Several detailed discussions of the spectra of amine-boranes and boron cations have been reported,<sup>4,27,28</sup> and are consistent with the findings in this study.

### Nuclear Magnetic Resonance Spectra

Proton nmr spectra of materials reported in this study were obtained on the Varian-A60 instrument, with tetramethylsilane (TMS) as an internal reference. The sodium salt of tetramethylsilylpropionate (TMSP) was used as an internal reference with  $D_2O$ . In most cases, methylene chloride or acetonitrile were the solvents of choice, but occasionally other solvents, such as nitromethane, or  $D_2O$ , were used in order to obtain more highly resolved spectra, when the compound was found to be less soluble in methylene chloride or acetonitrile. The chemical shifts,  $\delta$ , in parts per million, and coupling constants,  $J$ , in Hertz, of proton resonances and boron resonances are reported in Tables V-VIII. The integrated intensities of the proton spectra of the compounds reported, agreed well with the expected values, and thus, nmr proved to be an extremely useful tool for characterization of the compounds prepared in this study.

Figure I

Electronic Spectrum of the Anhydro Base of  
2,2'-Dipyridylmethanedihydroboron (1+) Chloride

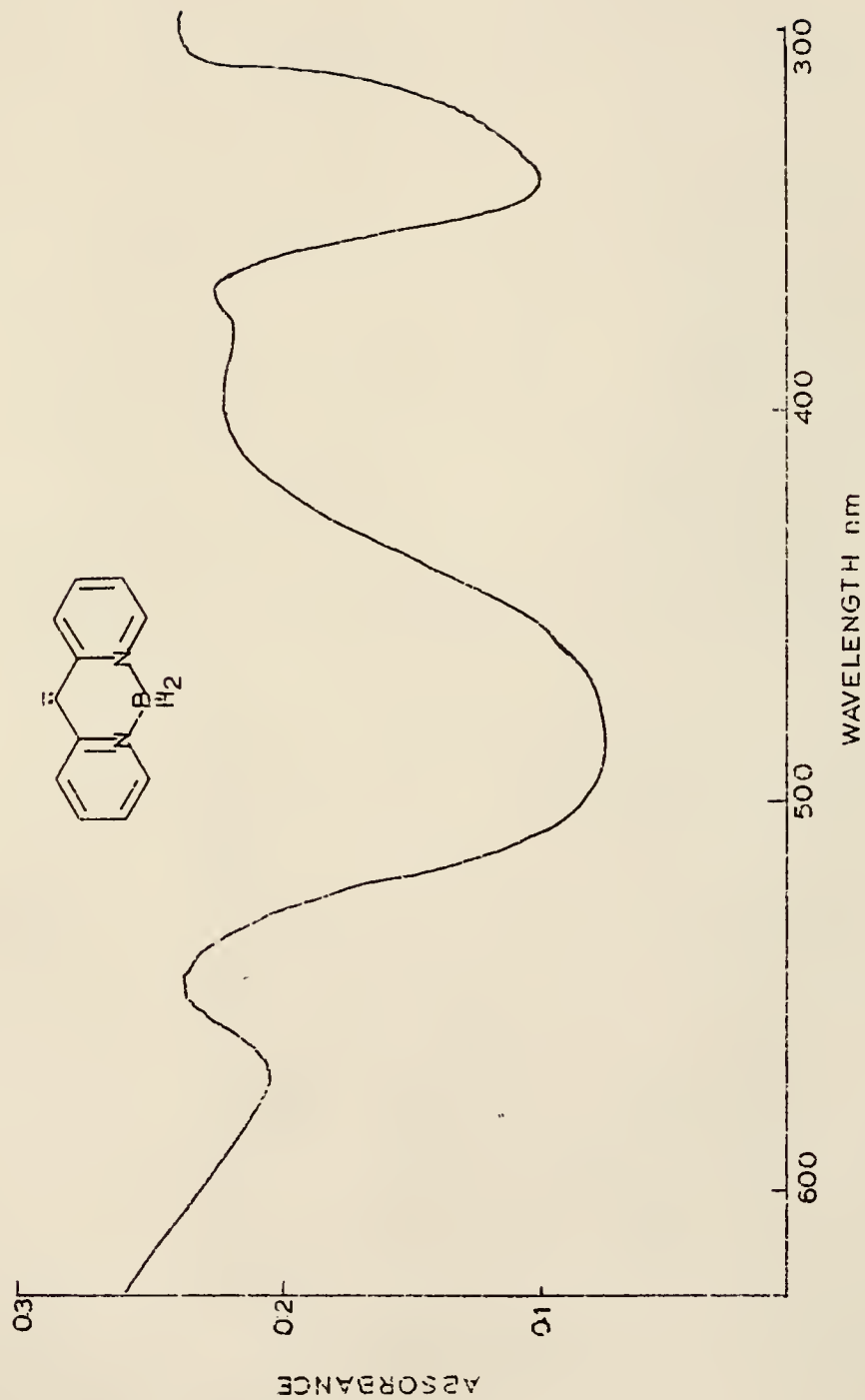


Table IV

Acid Base Equilibrium Data of 2,2'-Dipyridylmethanedihydroboron (1+) Chloride

Solution number	pH	$T_{368 \text{ nm}}$	$(\text{cm}^{-1} \text{ m}^{-1}) \times 10^2$	$K_a \times 10^{-13}$
1	2.01	1.00	0.00	-----
2	11.60	0.630	9.98	7.49
3	11.61	0.631	9.95	7.29
4	11.59	0.642	9.58	7.27
5	11.60	0.635	9.81	7.33
6	11.94	0.134	43.43	-----

Total Conc. Absorbing Species =  $2.01 \times 10^{-4} \text{ M}$  $\lambda = 368 \text{ nm}$ Average  $K_a = 7.35 \pm 0.11 \times 10^{-13}$ ,  $\text{p}K_a = 12.13$

Table V

Proton NMR Data of 2,2'-Dipyridylmethane and Derivatives

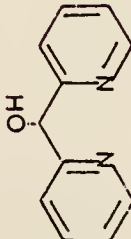
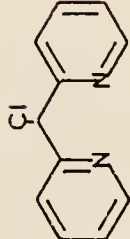


Compound	Solvent	Aliphatic $\delta$ ppm	Aromatic $\delta$ ppm
	$\text{CCl}_4$	-5.88(d, 2, CH-OH)	-6.94(m, 2, H-3, 3') -7.47(m, 4, H-4-4', 5-5')
	$\text{CCl}_4$	-6.12(s, 1, CH)	-7.09(m, 2, H-3-3') -7.60(m, 4, H-4-4', 5-5') -8.49(m, 2, H-6-6')
	$\text{CCl}_4$	-4.21(s, 2, CH <sub>2</sub> )	-7.19(m, 6, H-3-3', 4-4', 5-5') -8.42(m, 2, H-6-6')
	$\text{CCl}_4$	-5.81(s, 1, CH)	-7.25(m, 9, H-3-3', 4-4', 5-5') -8.40(m, 3, H-6-6')

Table V (continued)

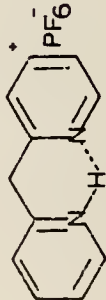
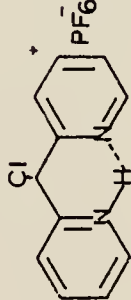
Compound	Solvent	Aliphatic $\delta$ ppm	Aromatic $\delta$ ppm
	$\text{CH}_3\text{CN}$	-4.60(s, 2, $\text{CH}_2$ )	-7.67(m, 4, H-3-3', 5-5') -8.15(m, 2, H-4-4') -8.31(m, 2, H-6-6')
	$\text{CH}_3\text{CN}$	-6.60(s, 1, CH)	-7.85(m, 4, H-3-3', 5-5') -8.31(m, 2, H-4-4') -8.80(m, 2, H-6-6')

Table VI

Proton NMR Data of Polyamine-Boranes

Compound	Solvent	Aliphatic $\delta$ ppm	Aromatic $\delta$ ppm
$\text{Me}_2\text{N}(\text{CH}_2)_2\text{NMe}_2 \cdot 2\text{BH}_3$	$\text{CH}_3\text{CN}$	-2.58(s, 12, $\text{CH}_3$ ) -3.14(s, 4, $\text{CH}_2$ )	
$\text{Me}_2\text{N}(\text{CH}_2)_2\text{NMe}_2 \cdot 2\text{BH}_3$	$\text{CH}_3\text{CN}$	-2.53(s, 12, $\text{CH}_3$ )	



Table VI (continued)

Compound	Solvent	Aliphatic $\delta$ ppm	Aromatic $\delta$ ppm
$\text{Me}_2\text{N}(\text{CH}_2)_4\text{NMe}_2 \cdot 2\text{BH}_3$	$\text{CH}_3\text{CN}$	-2.50(s, 12, $\text{CH}_3$ )	
$\text{Me}_2\text{N}(\text{CH}_2)_6\text{NMe}_2 \cdot 2\text{BH}_3$	$\text{CH}_2\text{Cl}_2$	-1.57(m, 12, $\text{CH}_2$ ) -2.52(s, 12, $\text{CH}_3$ )	
$\text{Me}_2\text{N}\overset{\text{Me}}{\underset{ }{\text{CH}}}_2\text{CHCH}_2\text{NMe}_2 \cdot 2\text{BH}_3$	$\text{CD}_3\text{CN}$	-2.60(s, 12, $\text{CH}_3$ ) -1.21(d, 3, $\text{CH}_3$ ) -2.67(m, 5, $\text{CH}$ , $\text{CH}_2$ )	
$\text{Me}_2\text{N}\overset{\text{Me}}{\underset{ }{\text{CH}}}\text{CH}_2\text{NMe}_2 \cdot 2\text{BH}_3$	$\text{CH}_2\text{Cl}_2$	-1.55(d, 3, $\text{CH}_3$ ) -2.48(s, 3, $\text{CH}_3$ ) -2.65(m, 9, $\text{CH}_3$ ) -3.36(m, 3, $\text{CH}$ , $\text{CH}_2$ )	
$\text{Me}_2\text{N}(\text{CH}_2)_2\overset{\text{Me}}{\underset{ }{\text{N}}}(\text{CH}_2)_2\text{NMe}_2 \cdot 3\text{BH}_3$	$\text{CH}_2\text{Cl}_2$	-2.65(s, 15, $\text{CH}_3$ ) -3.21(s, 8, $\text{CH}_2$ )	

Table VI (continued)

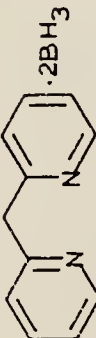

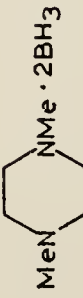
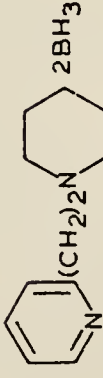
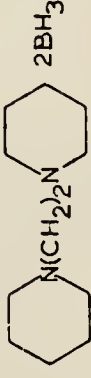
Compound	Solvent	Aliphatic $\delta$ ppm	Aromatic $\delta$ ppm
	$\text{CH}_3\text{CN}$	-5.90(s, 2, $\text{CH}_2$ )	-7.15(m, 2, H-3-3') -7.50(m, 2, H-5-5') -7.98(m, 2, H-4-4') -8.78(m, 2, H-6-6')
	$\text{CH}_3\text{CN}$		-7.66(m, 4, H-3-3', 5-5') -8.11(m, 2, H-4-4') -8.83(m, 2, H-6-6')
	$\text{CH}_2\text{Cl}_2$	-2.17(s, 6, $\text{CH}_3$ ) -3.10(m, 8, $\text{CH}_2$ )	
	$\text{CH}_2\text{Cl}_2$	-1.67(m, 6, $\text{CH}_2$ ) -3.00(m, 4, $\text{CH}_2$ ) -3.70(m, 4, $\text{CH}_2$ )	-7.38(m, 2, H-3-5) -7.89(m, 1, H-4) -8.65(m, 1, H-6)
	$\text{CH}_2\text{Cl}_2$	-1.66(m, 12, $\text{CH}_2$ ) -2.83(m, 8, $\text{CH}_2$ ) -3.14(s, 4, $\text{CH}_2$ )	

Table VI (continued)

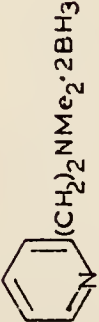
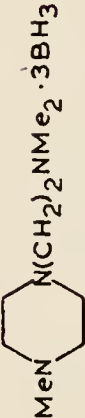
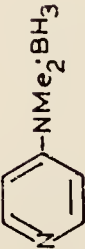
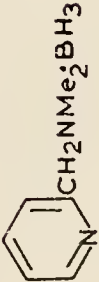
Compound	Solvent	Aliphatic $\delta$ ppm	Aromatic $\delta$ ppm
	$\text{CH}_2\text{Cl}_2$	-2.65 (s, 6, $\text{CH}_3$ ) -3.88 (m, 2, $\text{CH}_2$ ) -3.65 (m, 2, $\text{CH}_2$ )	-7.48 (m, 2, H-3-5) -7.90 (m, 1, H-4) -8.67 (m, 1, H-6)
	$\text{CH}_2\text{Cl}_2$	-2.64 (s, 9, $\text{CH}_3$ ) -2.84 (m, 6, $\text{CH}_2$ ) -3.42 (m, 6, $\text{CH}_2$ )	
	$\text{CH}_2\text{Cl}_2$	-3.03 (s, 6, $\text{CH}_3$ )	-6.46 (m, 2, H-3-5) -7.93 (m, 2, H-2-6)
	$\text{CH}_2\text{Cl}_2$	-2.60 (s, 6, $\text{CH}_3$ ) -4.03 (s, 2, $\text{CH}_2$ )	-7.30 (m, 2, H-3-5) -7.71 (m, 1, H-4) -8.60 (m, 1, H-6)



Table VII (continued)

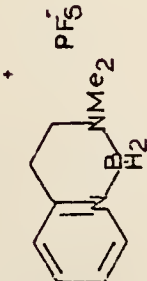
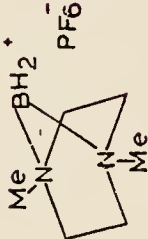
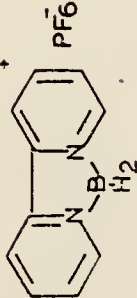
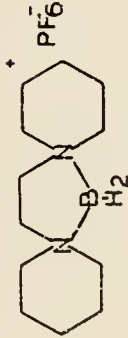

Compound	Solvent	Aliphatic $\delta$ ppm	Aromatic $\delta$ ppm
	$\text{CH}_2\text{Cl}_2$	-2.77 (s, 6, $\text{CH}_3$ )	-7.63 (m, 2, H-3, 5) -8.03 (m, 1, H-4) -8.18 (m, 1, H-6)
	$\text{CH}_2\text{Cl}_2$	-2.77 (s, 6, $\text{CH}_3$ ) -3.44 (s, 8, $\text{CH}_2$ )	
	$\text{CH}_3\text{CN}$		-7.98 (m, 2, H-3-3') -8.53 (m, 4, H-4-4', 5-5') -8.83 (m, 2, H-6-6')
	$\text{CH}_2\text{Cl}_2$	-1.73 (m, 12, $\text{CH}_2$ ) -3.41 (s, 4, $\text{CH}_2$ )	
	$\text{CH}_2\text{Cl}_2$	-1.78 (m, 6, $\text{CH}_2$ ) -3.03 (m, 4, $\text{CH}_2$ ) -3.46 (s, 4, $\text{CH}_2$ )	-7.62 (m, 2, H-3-5) -8.21 (m, 2, H-2-4)

Table VII (continued)

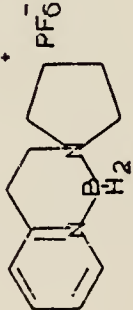
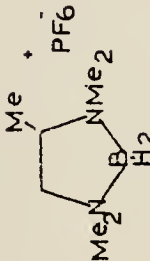
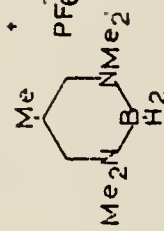
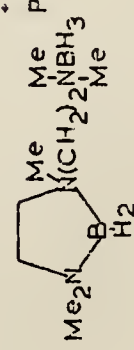
Compound	Solvent	Aliphatic $\delta$ ppm	Aromatic $\delta$ ppm
	$\text{CH}_2\text{Cl}_2$	-2.15(m, 4, $\text{CH}_2$ ); -3.49(s, 4, $\text{CH}_2$ )	-7.67(m, 2, H-3-5) -8.17(m, 2, H-2-4)
	$\text{CH}_2\text{Cl}_2$	-1.34(d, 3, $\text{CH}_3$ ); -2.76(s, 3, $\text{CH}_3$ ); -3.48(m, 1, $\text{CH}_2$ );	-2.66(s, 3, $\text{CH}_3$ ) -2.88(s, 6, $\text{CH}_3$ ) -3.51(m, 2, $\text{CH}_2$ )
	$\text{CD}_3\text{CN}$	-0.95(d, 3, $\text{CH}_3$ ); -2.83(s, 6, $\text{CH}_3$ );	-2.66(s, 6, $\text{CH}_3$ ) -2.68(m, 5, $\text{CH}_2$ )
	$\text{CD}_3\text{CN}$	-2.60(s, 6, $\text{CH}_3$ ); -2.86(s, 6, $\text{CH}_3$ ); -2.92(m, 4, $\text{CH}_2$ )	-2.82(s, 3, $\text{CH}_3$ ) -3.51(s, 4, $\text{CH}_2$ )

Table VII (continued)

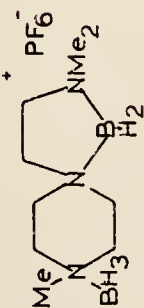
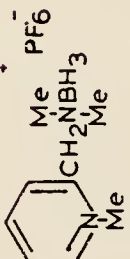
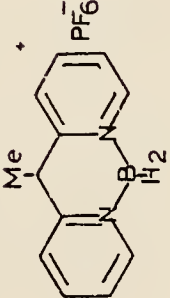
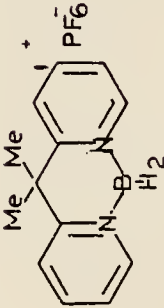
Compound	Solvent	Aliphatic $\delta$ ppm	Aromatic $\delta$ ppm
	CD <sub>3</sub> CN	-2.68(s, 3, CH <sub>3</sub> ); -2.85(s, 6, CH <sub>3</sub> ) -3.08(m, 4, CH <sub>2</sub> ); -3.52(m, 8, CH <sub>2</sub> )	
	CD <sub>3</sub> CN	-2.78(s, 6, CH <sub>3</sub> ) -4.38(s, 2, CH <sub>2</sub> ) -4.58(s, 2, CH <sub>2</sub> )	-8.08(m, 2, H-3-5) -8.48(m, 1, H-4) -8.74(m, 1, H-6)
	CH <sub>2</sub> Cl <sub>2</sub>	-1.95(d, 3, CH <sub>3</sub> ) -4.60(m, 1, CH)	-7.85(m, 2, H-3-3') -8.35(m, 4, H-4-4', 5-5') -8.69(m, 2, H-6-6')
	DMSO d <sub>6</sub>	-1.93(s, 6, CH <sub>3</sub> )	-7.99(m, 2, H-3-3') -8.50(m, 4, H-4-4', 5-5') -8.97(m, 2, H-6-6')



Table VII (continued)

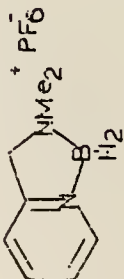
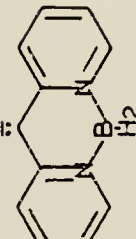
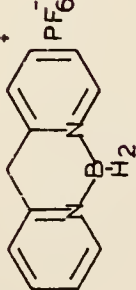
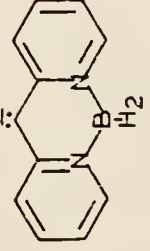
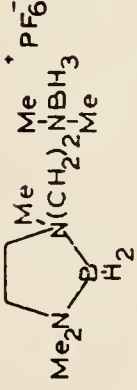
Compound	Solvent	Aliphatic $\delta$ ppm	Aromatic $\delta$ ppm
	$\text{CH}_2\text{Cl}_2$	-2.96(s, 6, $\text{CH}_3$ ); -4.71(s, 2, $\text{CH}_2$ )	-7.83(m, 2, H-3-5) -8.30(m, 1, H-4) -8.50(m, 1, H-6)
	$\text{CCl}_4$	-4.93(s, 1, CH)	-6.28(m, 4, H-3-3', 5-5') -6.97(m, 2, H-4-4') -7.30(m, 2, H-6-6')

Table VIII  
 $^{11}\text{B}$  Data

Compound	Solvent	Chemical Shift $\delta$ ppm	Mult.	$J_{\text{B-H}}$ Hz
	$\text{CH}_3\text{CN}$	23.1	3	110
	$\text{CH}_2\text{Cl}_2$	22.9	3	100
	$\text{CH}_3\text{CN}$	13.7 28.8	3 4	108 96

## CHAPTER VII

### DISCUSSION

#### 2,2'-Dipyridylmethane and Derivatives

The chemistry of 2,2'-dipyridylmethane and its derivatives has received only meager attention in the literature, in spite of their attractiveness as coordinating ligands. One explanation might be their lack of commercial availability, and the poor synthetic methods available for their preparation.

The literature describes several methods for the synthesis of 2,2'-dipyridylmethane,<sup>12-16,35</sup> however, attempts to duplicate these methods resulted in poor yields and considerable by-products that made purification extremely difficult. Thus, reported methods of synthesis did not provide a convenient source of starting material for this study.

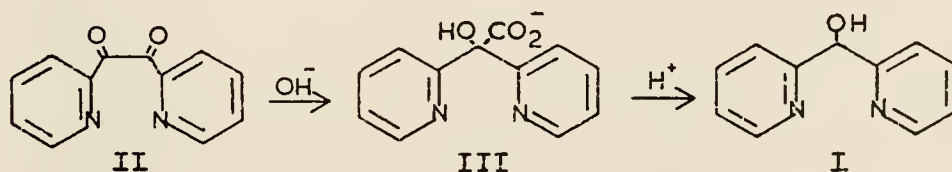
The reported oxidation of 2,2'-dipyridylmethane to 2,2'-dipyridylketone<sup>13</sup> suggested that the reduction of 2,2'-dipyridylketone to 2,2'-dipyridylmethane might be a plausible route to the desired material. The lack of reactivity of the ketone toward reduction to 2,2'-dipyridylmethane, by classical means, was reported in the literature<sup>16</sup> and attempts in this study confirmed this report. This lack of reactivity is surprising, since the reduction of benzo-

phenone, which is isoelectronic to 2,2'-dipyridylketone, undergoes reduction easily to diphenylmethane. The decreased reactivity is accounted for either in terms of reaction of the pyridine nitrogens with Lewis acid reagents employed in many reductions (i.e.  $\text{ZnCl}_2/\text{HCl}$ ,  $\text{AlCl}_3/\text{LiAlH}_4$ ), resulting in deactivation through inductive effects, or the reactivity of the pyridine ring to commonly employed reagents (i.e.  $\text{LiAlH}_4$ ,  $\text{NaOH}$ ). However, the ready availability of 2,2'-dipyridylketone prompted further study of its conversion to 2,2'-dipyridylmethane, and a three step synthetic pathway was developed.

Reduction of 2,2'-dipyridylketone to 2,2'-dipyridylmethanol(I) is accomplished quantitatively with sodium borohydride in aqueous solution.



An alternative method investigated for the synthesis of 2,2'-dipyridylmethanol was that reported by Klosa,<sup>19,20</sup> in which 2,2'-pyridil(II) was reacted with sodium hydroxide in methanol to produce 2,2'-pyridilate(III) and then decarboxylated with acid to 2,2'-dipyridylmethanol(I).<sup>19,20</sup>



The yield was considerably lower than that reported,<sup>20</sup> but

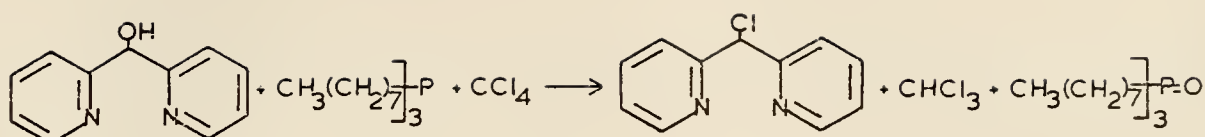
the low cost and availability of 2,2'-pyridil made this procedure attractive, especially if large quantities of 2,2'-dipyridylmethanol were desired.

The isolated and characterized 2,2'-dipyridylmethanol from this reaction could be converted to the chloride derivative with thionyl chloride, as described previously.<sup>16</sup> The yield, however, was low and unsuitable in this study.

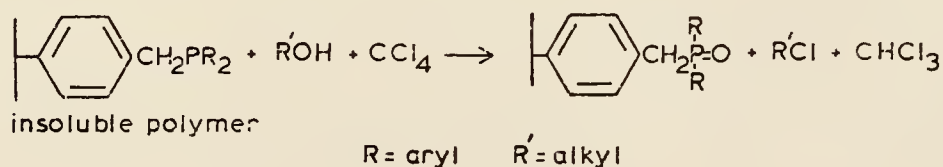
Attempted conversion of the alcohol to the chloride derivative, analogous to the conversion of benzhydrol to benzhydryl chloride, with concentrated hydrochloric acid, failed to produce the desired product. The failure of this reaction is accounted for by the reaction of the pyridine nitrogens with hydrochloric acid, yielding a (2+) ammonium salt. This would reduce the potential charge stabilization of the incipient carbonium ion, or prevent protonation at the OH group prior to substitution.

The utility of a procedure, reported by several workers,<sup>36,37</sup> for the conversion of primary and secondary alcohols to the corresponding chlorides or bromides, by reaction of the alcohol with a trialkyl or triarylphosphine, and carbon tetrachloride or carbon tetrabromide, was investigated.

The isolation and characterization of previously uncharacterized 2,2'-dipyridylchloromethane, in high yield, was accomplished by the reaction of 2,2'-dipyridylmethanol with tri-n-octylphosphine in carbon tetrachloride.



One minor complication in the reaction is the separation of the chloride derivative from a suspension of carbon tetrachloride, tri-n-octylphosphine oxide, and chloroform. The use of additional chloroform in the work up was applied with good results, but does require considerable effort. Recently, there was reported an insoluble, polymeric, styrene-based phosphine, which has the same reaction properties toward alcohols as monomeric analogs in carbon tetrachloride.<sup>38</sup> Employment of this reagent would eliminate the presence of phosphine oxide in solution, and should eliminate the separation problem, since the solution, as shown, would contain only chloroform, carbon tetrachloride, and the alkyl chloride:



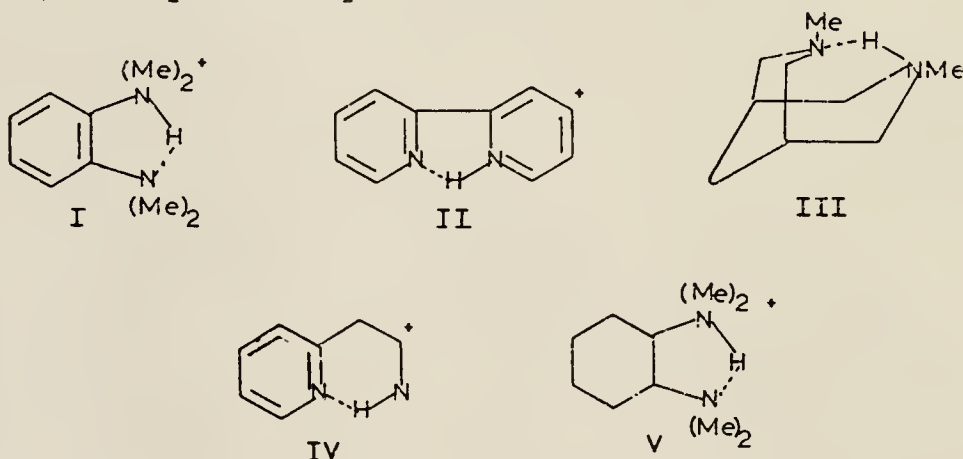
The polymeric phosphine oxide can be reduced and recovered for reuse.

Conversion of 2,2'-dipyridylchloromethane to 2,2'-dipyridylmethane in high yield, was accomplished by reduction with zinc metal in hydrochloric acid solution. The synthesis

of 2,2'-dipyridylmethane, in high yields, was also accomplished from 2,2'-dipyridylketone, employing the reactions described above without isolation of the various intermediates.

### Ammonium (1+) Salts

The ability of certain 1,2- and 1,3-diamines to form stable ammonium (1+) salts with strong mineral acids, appears to be determined largely by steric factors. An example of this behavior is found in the report of Alder and co-workers,<sup>39</sup> that 1,8-bis(dimethylamino)naphthalene forms a very stable ammonium (1+) salt. Douglass and co-workers,<sup>17</sup> also reported the synthesis and characterization of stable ammonium (1+) salts from 1,2-bis(dimethylamino)benzene(I), 2,2'-bipyridine(II), 2-(2-dimethylaminoethyl)pyridine(IV), 3,7-dimethyl-3,7-diazabicyclo 3.3.1 nonane(III), and trans-1,2-bis(dimethylamino)cyclohexane(V).



The diamines 2,2'-dipyridylmethane and 2,2'-dipyridylchloromethane are relatively rigid molecules, which upon protonation possess very favorable geometry for intramolec-



ular hydrogen-bonding, and it was not unexpected that they also form stable ammonium (1+) salts.

In the synthesis of the ammonium (1+) hexafluorophosphate salts of 2,2'-dipyridylmethane and 2,2'-dipyridylchloromethane, it is of interest to note that under very acidic (pH=1) conditions, a water insoluble salt is not obtained, but when the pH of the solution is increased to approximately 4, the insoluble ammonium (1+) salt precipitates. The increased solubility of the ammonium (2+) salt, which would be expected under very acidic conditions, provides for a convenient separation. The ammonium (2+) salt of 2,2'-dipyridylmethane, isolated from an organic medium with HBr gas, was not stable in aqueous solution. Attempted recrystallization from water resulted in the loss of one mole of acid to form the ammonium (1+) salt.

#### 2,2',2''-Tripyridylmethane

The only report to date on 2,2',2''-tripyridylmethane was the isolation as a reaction by-product, from the reaction of 2-picolyllithium and 2-bromopyridine, in 25.1% yield. The material was assumed to have the structure of 2,2',2''-tripyridylmethane.<sup>14</sup> It is of interest that no further attempts to characterize or employ the material as a tridentate ligand have appeared.

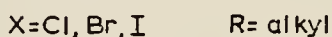
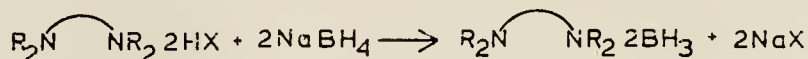
A pure sample of 2,2',2''-tripyridylmethane was isolated and characterized in good yield from the reaction of 2,2'-dipyridylmethane, with phenyllithium and 2-bromopyridine.

Although studies of its coordination chemistry were not undertaken, its structure and expected reactivity, based on the findings of this study suggest that it would possess similar properties to those described for 2,2'-dipyridylmethane.

### Polyamine-Boranes

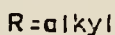
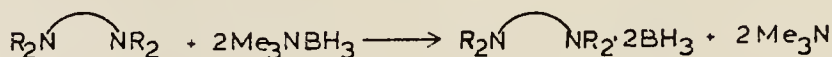
Borane adducts of polyamines containing two or more tertiary nitrogen atoms, were prepared in essentially quantitative yield, by three apparently general synthetic methods.<sup>21-24</sup>

Method 1 involves the reaction of sodium borohydride and acid salts of polyamines in dry, peroxide-free monoglyme, as described by the following equation:



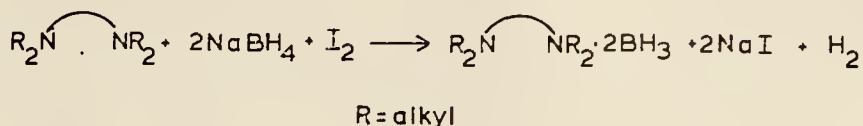
It is imperative that peroxide-free monoglyme be used, because the reaction of diborane with peroxides reduces yields.

Method 2 involves the reaction of polyamines with trimethylamine-borane in a transamination reaction, as described by the following equation:



It is necessary to continuously remove the trimethylamine in order to drive the reaction to completion.

Method 3 involves the reaction of polyamines with sodium borohydride and iodine in dry monoglyme, as described by the following equation:



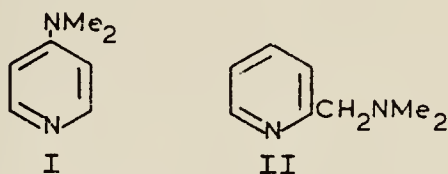
The removal of sodium iodide from the amine-borane often complicates the work-up, unless the amine-borane is insoluble in water, thus facilitating easy removal of sodium iodide by aqueous extraction.

Of the three methods, the preferred is the reaction of sodium borohydride with the ammonium salts of polyamines. The preference is based on short reaction times, high yields, and easy removal of the borane. However, the limitation to this reaction is that many polyamines do not produce anhydrous ammonium salts suitable for this reaction, and often considerable work is required in their preparation.

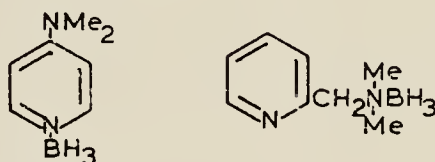
Selection of the method of synthesis for the polyamine-boranes reported in this study was based on their structure, relative base strengths, and ability to produce suitable ammonium salts. In general, all polyamines which did not produce suitable ammonium salts were reacted according to their base strength, with aliphatic polyamines subjected to the transamination reaction and aromatic polyamines, or mixed (aromatic-aliphatic) amines, subjected to the sodium borohydride iodine reaction.

The borane adducts of the various polyamines prepared in this study are white, crystalline solids. In general, they all have some solubility in methylene chloride, benzene, nitromethane, acetonitrile, and monoglyme. The polyamine boranes are, however, less soluble than mono-adducts in the same solvent.

Of the polyamines investigated, only 4-N,N-dimethylamino-pyridine (I), and 2-(N,N-dimethylaminomethane)pyridine (II) failed to yield borane adducts on each available nitrogen.

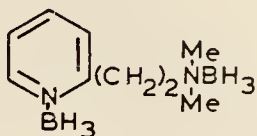


The mono-borane adducts of each were obtained and assigned the following structures:

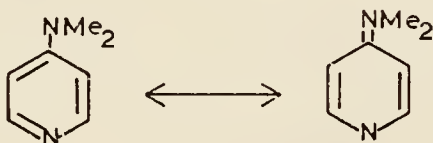


The structure assignments were based on proton nmr spectra and cationic derivatives, which will be discussed later in this chapter. The lack of reactivity of the second nitrogen atom in both diamines is accounted for in terms of their reduced base strength, resulting from the electronic effects of the attached dimethylamino groups. It was observed that as the dimethylamino group is moved further away from the ring, the base strength of the second nitrogen toward reaction with

diborane is increased. For example, 2-(-N,N-dimethylamino-ethane)pyridine-bis(borane) was obtained under equivalent conditions.



The attachment of the borane ( $\text{BH}_3$ ) group on the pyridine nitrogen in 4-(-N,N-dimethylamino)pyridine, instead of the dimethylamino nitrogen  $[\text{CH}_3]_2\text{N}$ , is accounted for by the increased base strength of the pyridine nitrogen, due to resonance delocalization of the electron pair from the dimethylamino group into the ring.



When the dimethylamino group is removed from the ring by one carbon atom, this resonance delocalization is no longer available, and borane ( $\text{BH}_3$ ) attachment to the more basic dimethylamino group is observed.

#### Cyclic Boronium Cations

The boron cations in this study form sparingly water-soluble salts with large anions, such as  $\text{PF}_6^-$ ,  $\text{AsF}_6^-$ ,  $\text{B}(\text{C}_6\text{H}_5)_4^-$ ,  $\text{B}_{12}\text{H}_{12}^{2-}$ ,  $\text{Br}_3^-$ , complex iodomercures  $\text{HgI}_3^-$  or  $\text{HgI}_4^{2-}$ . By metathetical reaction, boronium iodides could be

converted to these less soluble derivatives, and the general details of conversion of boronium iodides to hexafluorophosphates were described in Chapter III. The high yields of boronium hexafluorophosphates, obtained from boronium iodides by metathetical reaction (Table III), show that the iodides are substantially pure; in fact, the losses can be accounted for by the slight solubility of the boronium hexafluorophosphate in water. The boronium hexafluorophosphates were white crystalline solids, which could be readily recrystallized from methylene chloride ether mixture, acetone water mixture, or from hot aqueous solutions.

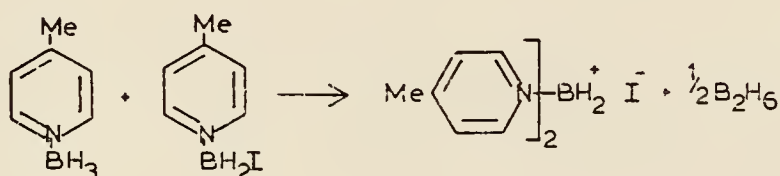
As reported previously, the chemistry of boron-nitrogen compounds have received considerable attention over the past decade.<sup>1</sup> One area of interest in the past several years has been the chemistry of bisamine boron cations,<sup>3,30</sup> and several workers have reported methods for incorporating this stable grouping into cyclic systems.<sup>26,40-42</sup>

The synthetic methods employed for the synthesis of cyclic boronium cations from polyamines are well described, and consist of numerous variations, providing considerable flexibility for their synthesis. However, application of these methods to the diamine 2,2'-dipyridylmethane failed to produce the desired cyclic boronium cation. This was quite surprising, since the synthesis of the cyclic boronium cation from 2,2'-dipyridylamine proceeded successfully by several of these methods. The failure of 2,2'-dipyridylmethane to behave as a typical diamine (reason to be discussed later

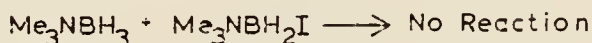


in this chapter) initiated the investigation for a new synthetic method for the synthesis of its cyclic boronium cation.

Concurrently with this study, McMaster<sup>18</sup> was investigating the kinetics of the reaction of amine-boranes with amine-iodoboranes, and reported that 4-methylpyridine-borane reacts with 4-methylpyridine-iodoborane in benzene to yield the bis-4-methylpyridine-boronium iodide and diborane.



McMaster also reported that when trimethylamine-borane and trimethylamine-iodoborane were heated together in benzene for several days, no cationic material was obtained.

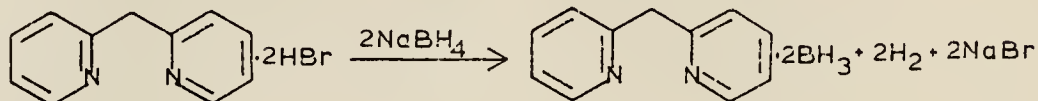


This lack of reactivity was also demonstrated in this study. From the above results, it appeared as if the reaction was facilitated by the presence of the pyridine ring system. Comparison of the diamine, 2,2'-dipyridylmethane with the starting materials and cation produced in McMaster's investigation, suggested that the two systems are structurally quite similar, and that suitable conditions might exist for an intramolecular reaction to produce the desired cyclic

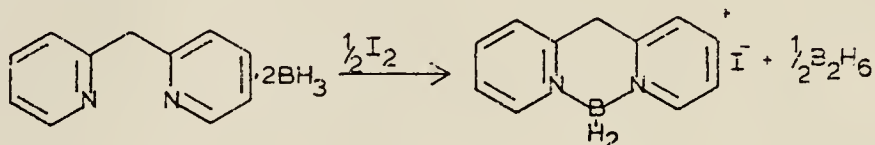


cation, assuming that the borane and iodoborane entities could be incorporated into the diamine.

Incorporation of the borane and iodoborane entities was accomplished by first synthesizing the bis(borane) from its ammonium (2+) bromide salt.



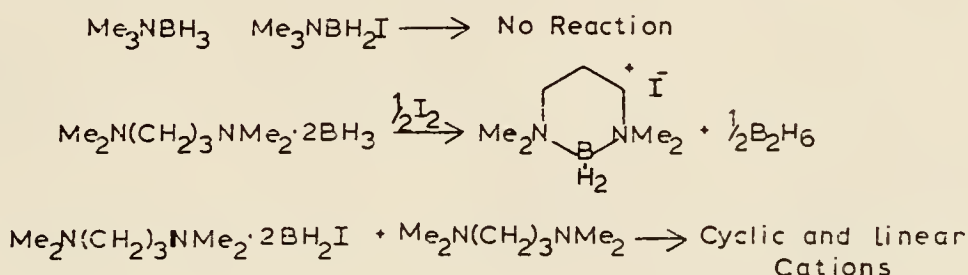
The reaction of this bis(borane) with an amount of iodine necessary to iodinate only one of the borane groups, yielded the desired cyclic boronium cation in high yield and purity, under mild conditions.



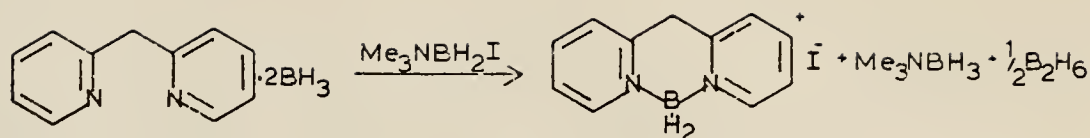
From the ease of synthesis, high yield, and purity of products, a study of this reaction was undertaken to investigate the possible general synthetic utility for cyclic boronium cation synthesis. A variety of polyamine-boranes of various tertiary diamines, synthesized by the methods reported in Chapter IV, were converted into cyclic boronium cations, as shown in Table (III).

It was of particular interest that cyclic boronium cations were easily obtained from aliphatic diamines such as N,N,N',N'-tetramethylethanediamine, and that no evidence for linear cation formation was obtained. This is noteworthy

in light of the lack of reaction between trimethylamine-borane and trimethylamine-iodoborane, even though the two systems are structurally quite similar, and in view of the results of Sullivan, who obtained a mixture of linear and cyclic cations when reacting the bis(iodoborane) of N,N,N',N',-tetramethylpropanediamine with N,N,N',N'-tetramethylpropanediamine.

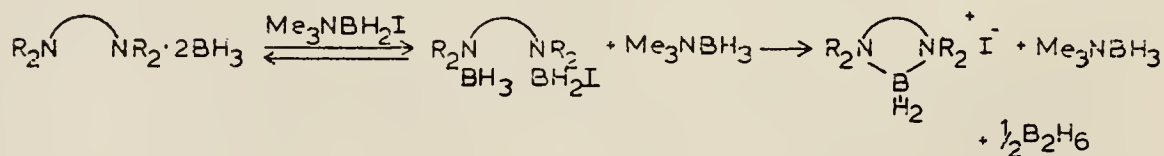
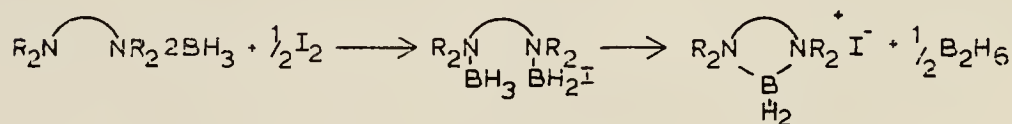


The ability of aliphatic tertiary diamine-bis(boranes) to produce exclusively cyclic boronium cations, when tertiary aliphatic monamine-boranes fail to produce linear boronium cations, suggests that the influence of the "chelate effect"<sup>43</sup> provides the additional driving force required for cation formation. The lack of reactivity to produce linear cations also provided an alternative to the use of iodine in the synthesis of cyclic boronium cations. In this case, the iodine could be replaced by an equivalent amount of trimethylamine-iodoborane, which undergoes an exchange reaction with the bis(borane), producing the cyclic boronium cation, and trimethylamine-borane; as illustrated below for the synthesis of 2,2'-dipyridylmethanedihydroboron (1+) iodide.



This procedure eliminates the presence of hydrogen iodide, a reaction intermediate when iodine is employed, which can undergo irreversible reactions with substrates possessing reactive nucleophilic sites. The use of iodine is the experimentally simpler of the two methods. However, trimethylamine-iodoborane provides an additional variation, which in this study was found to be useful with one polyamine-borane, in which the use of iodine caused problems due to the insolubility of intermediate salts formed.

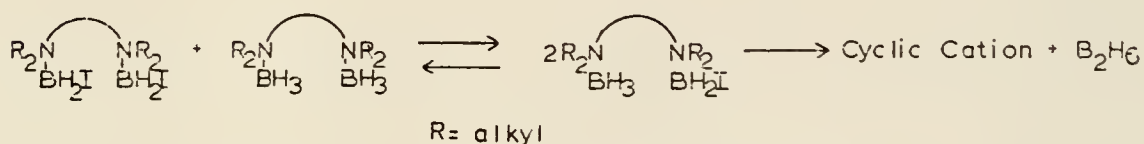
The following equations represent the general reaction sequence for the conversion of diamine-bis(boranes) into cyclic boronium cations.



R = alkyl

In the reaction with iodine, there must exist a rapid

exchange of borane ( $\text{BH}_3$ ), and iodoborane ( $\text{BH}_2\text{I}$ ), since in the synthetic procedure solid iodine is added rapidly, and since direct iodination is known to be very rapid, formation of bis(iodoborane) molecules is very likely. The redistribution reaction also appears to be rapid, as evidenced by the rapid rates of formation of some of the cations prepared by this method. However, the redistribution is considerably slower than iodination.



Additional evidence for exchange was found in the reactions employing trimethylamine-iodoborane, in which exchange must occur in order for reaction to proceed. The kinetics of this exchange reaction, as well as the mechanism by which cyclic boronium cations are formed, are currently under investigation in this laboratory. Several possibilities exist, but will not be discussed at this time.

It was observed that the rate of cation formation was very dependent upon both the structure of the diamine, and also whether or not it contained pyridine, tertiary aliphatic or mixed (pyridine, tertiary aliphatic) amines. In general, the order of reactivity observed for equivalent ring size of the boronium cation was pyridine diamines react faster than mixed (pyridine, tertiary aliphatic) diamines, and both react faster than tertiary aliphatic diamines. The

faster reaction of pyridine amines is easily accounted for in the established chemistry of boron cation synthesis: pyridine bases react with trimethylamine-iodoborane ( $(\text{CH}_3)_3\text{NBH}_2\text{I}$ ) much faster than do tertiary aliphatic amines.<sup>30</sup> On this basis, a pyridine-amine function in the molecule would be expected to react with an amine-iodoborane group faster than a tertiary aliphatic amine.

Reactivity orders observed for various ring sizes of the boronium cations were five-membered rings are formed faster than six-membered rings and six-membered rings are formed faster than seven-membered rings, as evidenced by the need for higher reaction temperatures to form a seven-membered ring boronium cation.

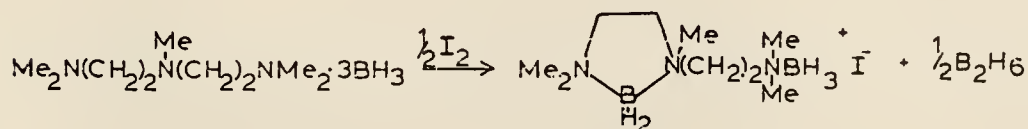
Work by Salomon<sup>44</sup> has shown that for a unimolecular cyclization of haloamines,  $\text{XCH}_2(\text{CH}_2)_n\text{NH}_2 \rightarrow (\text{CH}_2)_{n+1}\text{NH}_2^+$ ,  $\text{X}^-$ , the most favorable balance between activation energy ( $\Delta E_a$ ) and frequency factor ( $A$ ) was obtained for five-membered rings. Much slower formation ( $\sim 10^{-5}$ ) of the four-membered ring was attributed to a larger activation energy for this more highly strained ring system. That a six-atom ring was produced more slowly than the five-membered analogue was accounted for by a decrease in the pre-exponential frequency factor. Although the reaction studied by Salomon, and the synthesis of cyclic boronium cations in this study are different in the atomic identity of the reaction sites, the final products are isoelectronic and isosteric. This suggests that, nevertheless, similar steric factors may operate in both types of reactions.

Synthesis of an eight-membered cyclic boronium cation was not attempted because of the lack of availability of a suitable diamine. However, the synthesis of a nine-membered ring boronium cation was attempted, but no cation was observed after 4 weeks of refluxing in mesitylene. Therefore, the reaction procedure is applicable to the synthesis of five to seven, and possibly eight-membered cyclic boronium cations from tertiary aliphatic diamines. Cyclic boronium cations of eight atoms or larger could possibly be prepared from pyridine diamines because of their increased reactivity, but linear cations would also be expected.

#### Boronium Cations Containing Amine-Boranes

The reaction of diamine-bis(boranes) with iodine to form cyclic boronium cations, suggested that a similar reaction might occur with a symmetrical tris(borane), and that the final product would contain both boryl ( $\text{BH}_2^+$ ) and borane ( $\text{BH}_3$ ) entities. The triamine chosen for this investigation was pentamethyldiethylenetriamine, and conversion to the tris(borane) was accomplished as described in Chapter IV.

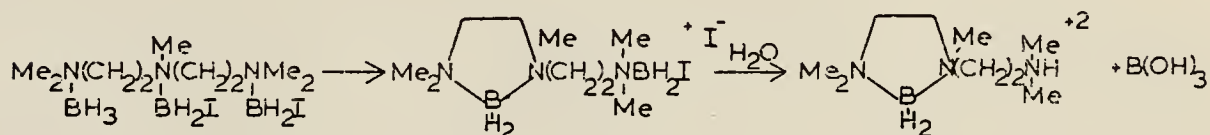
The reaction was initially carried out with an amount of iodine sufficient to convert only one borane ( $\text{BH}_3$ ) group per molecule into an iodoborane ( $\text{BH}_2\text{I}$ ). Thus, formation of a five-membered cyclic boronium cation with a pendant dimethylamino-borane was expected.



In the work-up of the iodide salt, it was observed that con-

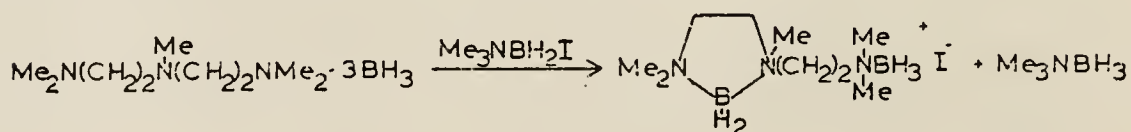


siderable gas evolution occurred, suggesting some type of decomposition. A proton nmr investigation of the reaction product (in D<sub>2</sub>O) revealed the presence of an ammonium salt, which is believed to have arisen from the aqueous decomposition of an iodoborane (BH<sub>2</sub>I) group present in the reaction product. The existence of such an impurity can easily be accounted for, since the reaction is carried out in a solvent in which the product is insoluble. The entrapment of some molecules containing an iodoborane group is likely if the molecule cyclizes while there are two iodoborane groups present on the molecule.

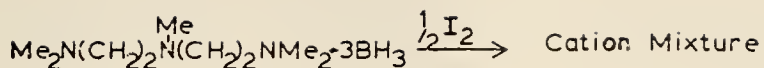


The insolubility of the iodoborane-containing cation prevents further exchange between iodoborane (BH<sub>2</sub>I) and borane (BH<sub>3</sub>) groups, hence, a mixture of reaction products results. Several attempts to separate and isolate the components of the reaction mixture were unsuccessful.

The synthesis of a pure sample of boryl (BH<sub>2</sub><sup>+</sup>) and borane (BH<sub>3</sub>) containing cation from pentamethyldiethylenetriamine was accomplished by the use of trimethylamine-iodoborane, rather than iodine.





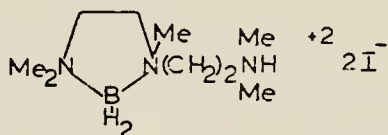


There was no evidence for any iodoborane-containing material or ammonium salt in the reaction product. The lack of any iodoborane impurity is accounted for in terms of a controlled ring closure reaction. If ring closure is faster or competitive with iodine exchange with trimethylamine-iodoborane, essentially no iodine would be incorporated into the product. Direct iodination is known to be very rapid and would be expected to produce random iodine substitution before ring closure, thus allowing for iodine incorporation in the product. The utility of trimethylamine-iodoborane was established in this reaction and offers additional control in synthesis of cyclic boronium cations.

Structure assignment was made by proton nmr and  $^{11}\text{B}$  nmr. The proton nmr revealed four singlets centered at -2.60 ppm, -2.82 ppm, -2.86 ppm, and -3.51 ppm, and a complex multiplet of low intensity covering the area from -2.50 ppm to -3.30 ppm, with an intensity ratio of 6:3:6:4:4, respectively. The four singlets correlate well with the given structure and represent the three different types of methyl hydrogens and the ring methylene hydrogens present in the molecule. Integral ratios are in good agreement with those expected. The chemical shift of the methylene hydrogens agreed well with

that of the cyclic boronium cation derived from N,N,N',N'-tetramethylethane-diamine. The multiplet was assigned to the nonequivalent methylene protons of the N,N-dimethyl-aminoethane substituent. The presence of the boryl ( $\text{BH}_2^+$ ) and borane ( $\text{BH}_3$ ) groups was confirmed by  $^{11}\text{B}$  nmr, which revealed a triplet and quartet at 13.7 ppm and 28.8 ppm, from trimethylborate, respectively.

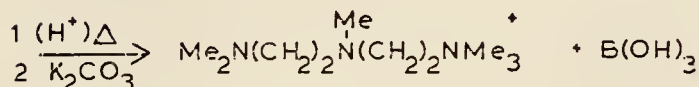
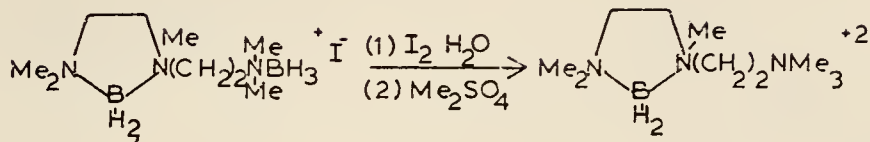
Assignment of the position of the borane ( $\text{BH}_3$ ) group was based on the general trend that methyl hydrogens of amine-boranes appear upfield with respect to analogous boronium cations. Removal of the borane ( $\text{BH}_3$ ) group with aqueous iodine revealed the loss of the singlet at -2.60 ppm, assigned to the amine-borane, and the appearance of a sharp singlet 19 Hz downfield. This new absorption is indicative of formation of the suspected ammonium ion.



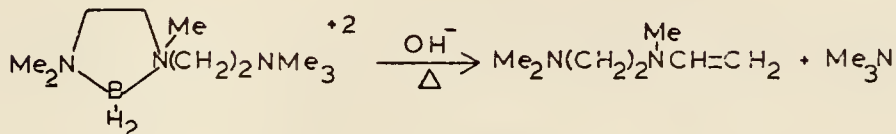
No attempt was made to isolate the material.

There exists an intriguing possibility of employing this chemistry as a template reaction for the functionalization of a particular amine group within a polyamine. The other amine sites are coordinated as a boronium cation, which when decomposed, yields a monofunctionalized polyamine.

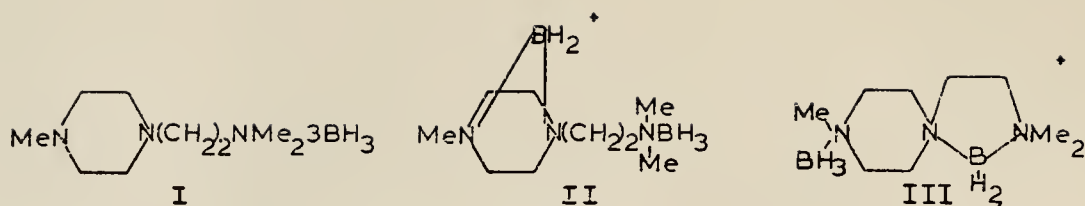
The following reaction proposals indicate several potential uses.



Or possibly:



The isolation of a cyclic boronium cation containing a borane group, from pentamethyldiethylenetriamine-tris(borane), should make possible further reactions of this type. For example, one interesting application was the potential selectivity of cyclic boronium cation formation in an unsymmetrical triamine-tris(borane). The predicted selectivity was based on formation rates reported earlier in this chapter, and was expected to result in formation of the most favorable ring size, when the triamine had unequal numbers of carbon atoms separating the nitrogen sites. The triamine-tris(borane) chosen for this investigation was N-methyl-N'-(2-dimethylaminoethyl)piperazine(I). The two possible ring closures are a seven-membered bicyclic ring (II), and a five-membered ring (III), as shown:

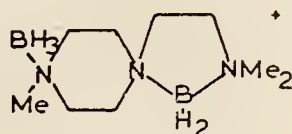


Comparison of the relative ease of formation of the bicyclic cation derived from N,N-dimethylpiperazine-bis(borane), and the five-membered cyclic cation from N,N',N'-tetramethylethylenediamine-bis(borane), suggested that the five-membered ring is more easily formed than the bicyclic ring, and would be favored in the triamine-tris(borane) reaction.

Synthesis of the cyclic boronium cation containing a borane ( $\text{BH}_3$ ) group, from N-methyl-N'-(2-dimethylaminoethyl)-piperazine-tris(borane), was accomplished through its reaction with iodine. No complication with ammonium salt formation was observed in this reaction, suggesting more favorable borane iodoborane exchange.

The proton nmr revealed two singlets centered at -2.80 ppm and -2.92 ppm, and two complex multiplets centered at -3.18 ppm and -3.66 ppm, with an intensity ratio of 3:6:4:8, respectively. The two singlets correlate well with the two types of non-coupling methyl hydrogens present in the molecule, and the two complex multiplets are assigned to the methylene hydrogens. Integral ratios are in good agreement with those expected for a five-membered ring cation. Comparison of the proton nmr with cations having structures similar to those proposed provided additional

support for a five-membered ring cation.

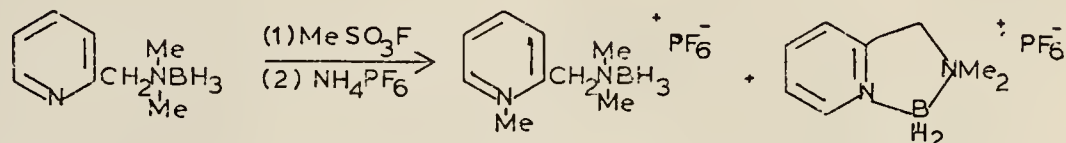


Assignment of the position of the borane ( $\text{BH}_3$ ) group was based on the general trend that methyl hydrogens of amine-boranes appear upfield with respect to analogous boronium cations. Therefore, the singlet at  $-2.80$  ppm was assigned to the amine-borane. The integral value of three hydrogens for this absorption supports the formation of the five-membered cyclic boronium cation, since the seven-membered bicyclic cation would require an integral value of six hydrogens for the dimethamino-borane group.

This structure assignment revealed the five-membered ring was selectively and exclusively produced over a bicyclic ring. This confirms the general hypothesis concerning differences in rates of formation of various ring sizes.

The boryl-borane ( $\text{BH}_2^+$ ,  $\text{BH}_3$ ) cations discussed above, represent a new class of boron-containing compounds not previously reported. The reactivity of iodine with the borane group in these cations suggest that considerable derivative chemistry could result from these materials through known reactions of amine-boranes. Thus, numerous structural variations might be introduced at the borane site. Work in this area was not attempted during this study.

The synthesis of another borane-containing cation resulted from the reaction of the mono(borane) derived from 2-(2-dimethylaminomethyl)pyridine, with methyl fluorosulfonate (Magic Methyl).



The presence of the cyclic boronium cation in the reaction was accounted for by a hydride abstraction from the borane group, by methyl fluorosulfonate. The use of hydride abstracting reagents, such as tritylchloride for boron cation synthesis has been reported.<sup>45,46</sup> Confirmation of the existence of the cyclic boronium cation, in the mixture, was obtained by synthesizing the cation via the reaction of the monoamine-borane, with tritylchloride. This resulted in a high yield of the cyclic boronium cation, whose properties correlated well with those of the cyclic boronium cation obtained in the methylation reaction above. Separation of the mixture from the methylation reaction was obtained by solubility differences of the hexafluorophosphate salts.

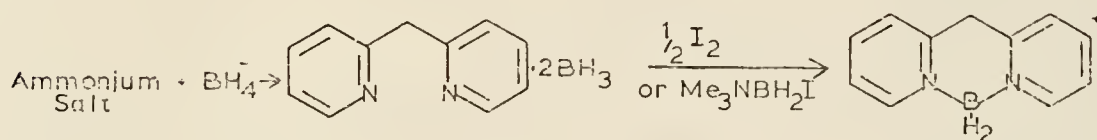
The proton nmr of the borane-containing cation revealed three upfield singlets with integral ratios of 6:2:3. The three singlets and integral values are in good agreement with the given structure. This evidence supports that the mono(borane) group is attached to the dimethylamino nitrogen and not the pyridine nitrogen, since the



latter would reveal only two singlets if the borane ( $\text{BH}_3$ ) group were attached to the pyridine nitrogen.

2,2'-Dipyridylmethanedihydroboron (1+),  
and Its Reactions

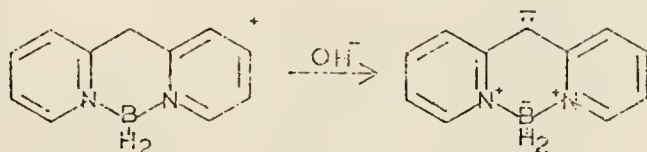
The synthesis of 2,2'-dipyridylmethanedihydroboron (1+) cation from 2,2'-dipyridylmethane-bis(borane) with either iodine or trimethylamine-iodoborane provided high yields of the cation.



The cation was characterized by elemental analysis, infrared, proton nmr,  $^{11}\text{B}$  nmr, and various derivatives.

Investigation of the physical properties of the cation demonstrated that the previously proposed enhanced reactivity of the bridging methylene hydrogens was, in fact, present. When the cation was reacted with bases, even as weak as pyridine, a deep red color was produced, which suggested a proton abstraction reaction.

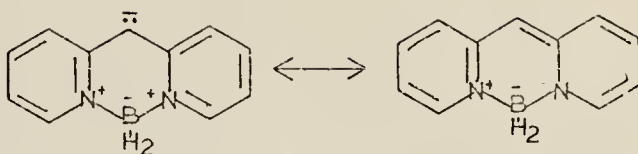
The deprotonation of the cyclic boronium cation of 2,2'-dipyridylmethane with aqueous sodium hydroxide easily produced an insoluble, intensely orange-colored, solid zwitterion.



The intense color is produced by the resonance delocalization

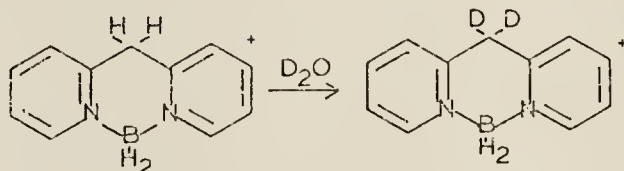


of the electron pair, providing for more extended conjugation in the molecule.



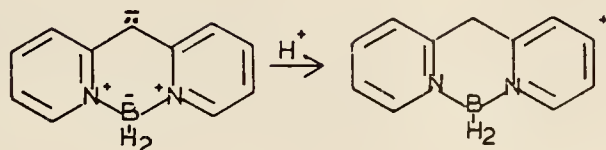
The enhanced reactivity of the bridging methylene hydrogens results from the inductive effect of the boryl ( $\text{BH}_2^+$ ) group. The formal positive charge that results when the diamine is coordinated to the boryl group exerts an electron withdrawing effect on the pyridine rings which reduces the electron density at the methylene hydrogens, and enhances stabilization of the resulting electron pair through resonance delocalization in the conjugate base.

Additional evidence supporting the enhanced reactivity of the bridging methylene hydrogens of 2,2'-dipyridyldihydroboron ( $1^+$ ) cation is found in the ability of the protons to rapidly exchange with deuterium in  $\text{D}_2\text{O}$ . A deuterated cation with 85% deuterium incorporation was obtained.

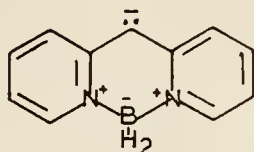


The reversibility of the deprotonation reaction, as evidenced by D-H exchange, was further demonstrated by

recovery of the parent cation upon protonation of the zwitterion with acid.



The proton nmr of the zwitterion obtained by deprotonation of 2,2'-dipyridylmethanedihydroboron cation is noteworthy.

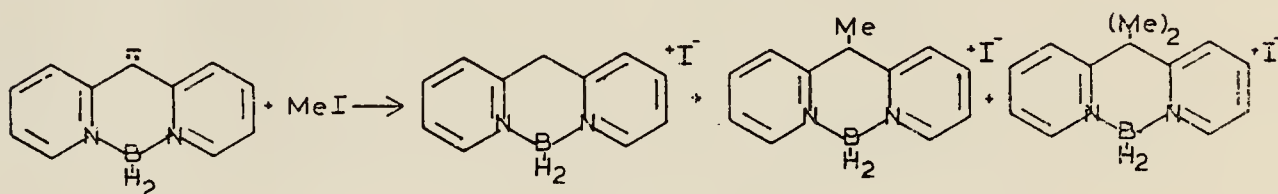


It revealed a downfield chemical shift of the lone methylene proton (-4.93 ppm) greater than that of the cyclic boronium cation (-4.68), suggesting that the lone-pair of electrons is considerably delocalized into the pyridine rings.

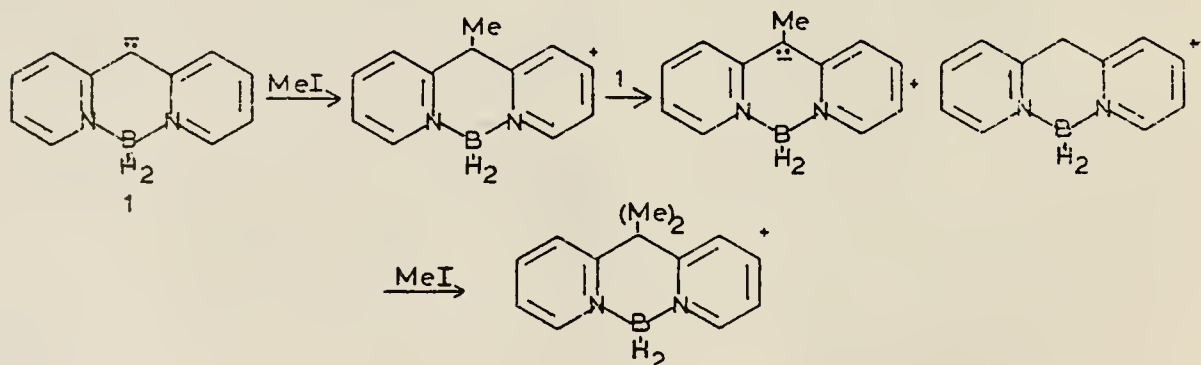
The intense red color produced on deprotonation of the cation provided a convenient colorimetric method for determining its pKa. The pKa was determined to be 12.13, supporting the acidic behavior of the cation toward various bases. During the determination of the pKa, it was observed that under alkaline conditions there was a slow reaction taking place, confirmed by a slow loss in intensity of the visible absorption band at 368 nm. The reaction was that of the zwitterion with dissolved oxygen in solution. Elimination of oxygen from the system prevented this reaction.

It was not surprising that the zwitterion reacts with oxygen, since it is known that auto-oxidation reactions of many organic molecules do occur under alkaline conditions.

One area of interest in the properties of the zwitterion was its potential use as a nucleophile. The proton nmr data indicated considerable delocalization of the electron pair, and suggested that the zwitterion's nucleophilicity should be decreased considerably. The nucleophilicity of the zwitterion was demonstrated by its reaction with methyl iodide.



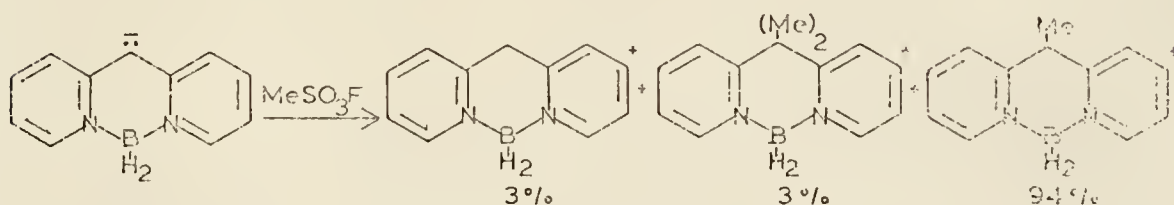
The reaction was very slow, which supports the expected weak nucleophilicity. From the product mixture it was evident that multiple reactions with methyl iodide had occurred. The presence of the parent cation (unsubstituted) supports a proton transfer reaction, and accounts for the formation of the dimethyl cation.



Production of the dimethyl cation suggests that there must

be little difference in the acidities of the unsubstituted and monomethyl cations. This is not surprising since the addition of a methyl substituent would not be expected to produce a significant change in the acidity constant of the cation.

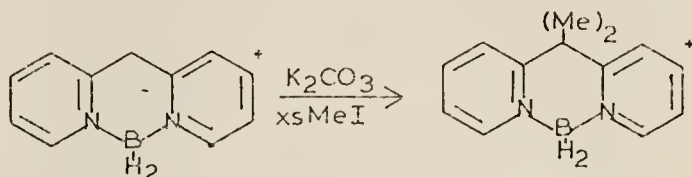
In an attempt to prepare exclusively monomethyl cation, a more powerful methylating agent (methylfluorosulfonate) was employed. The reaction was very rapid, and isolation of the reaction product revealed a mixture consisting of monomethyl cation (94%), dimethyl cation (3%), and unsubstituted cation (3%).



The ratio of dimethyl cation and unsubstituted cation establishes the equal participation of the monomethyl zwitterion and unsubstituted zwitterion. From the above results, it is evident that even when a powerful and rapid methylating agent is employed, the proton transfer between the monomethyl cation and zwitterion can still compete with methylation.

The facility of removal of a proton from the cation suggested that a dimethyl cation could be prepared by reaction of the cation with a methylating agent in the presence of a base, such as potassium carbonate or a non-

coordinating amine such as 1,8-bis(dimethylamino)naphthalene. The base provides for continuous removal of a proton and drives the reaction to completion, since the dimethyl cation has no remaining protons and is not reactive with the bases employed.



Another area of interest in the reactivity of the zwitterion was the potential of isolating a trigonal heteroaromatic boron cation by hydride abstraction from the boron atom. Attempts to prepare such a compound by the reaction of the zwitterion with tritylperchlorate, failed to yield any identifiable product other than triphenylmethane. However, the presence of triphenylmethane provides evidence for hydride abstraction. The insoluble nature of the crude reaction product, as well as its reactivity toward many common solvents, complicated the attempts to identify the material. No attempts to prepare derivatives from the crude reaction were undertaken, but this route could provide suitable evidence for the existence of the trigonal heteroaromatic cation.

#### Reaction of 2,2'-Dipyridylmethane with Trimethylamine-Iodoborane

The reaction of 2,2'-dipyridylmethane with trimethylamine-iodoborane produced a deep red solution which failed to yield a cyclic boronium cation.

The proton nmr of the reaction was monitored as a function of reaction time, and revealed a very complex reaction, as evidenced by the presence of several absorptions that could not be accounted for in terms of starting materials or expected products. Addition of base (NaOH) to the crude reaction product resulted in production of trimethylamine and 2,2'-dipyridylmethane.

The red color that results during the reaction is noteworthy. As previously described, the cyclic boronium cation of 2,2'-dipyridylmethane, obtained from the reaction of 2,2'-dipyridylmethane-bis(borane) and iodine, exhibits weak acid properties, and deprotonation of the cation results in deep red solutions. Thus, the red color observed in the reaction is attributed to deprotonation of a boronium cation formed in the reaction. It was confirmed that 2,2'-dipyridylmethane and trimethylamine produce deep red solutions when allowed to react with the cyclic boronium cation of 2,2'-dipyridylmethane. This provides evidence for their involvement in the reaction.

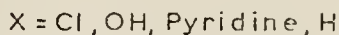
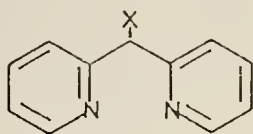
In the reaction, the first step is most likely cation formation by the displacement of iodide from trimethylamine-iodoborane by one of the nitrogens in 2,2'-dipyridylmethane. This intermediate cation could cyclize with loss of trimethylamine to form a cyclic boronium cation. Either cation would be susceptible to proton loss. It is likely that both cations are involved, as well as both amines (2,2'-dipyridyl-



methane and trimethylamine), in proton transfer reactions. However, other reactions must have occurred, as evidenced by the complex nmr spectrum of the solution. All attempts to separate the reaction mixture were unsuccessful.

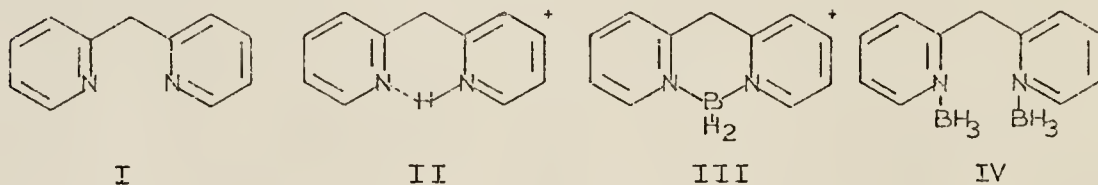
Nuclear Magnetic Resonance Correlations  
of 2,2'-Dipyridylmethane and Derivatives

It was of interest to compare the deshielding magnitude of various methylene substituents on the methylene hydrogen for various derivatives of 2,2'-dipyridylmethane.



As expected, the magnitude of deshielding follows the order  $\text{Cl} > \text{OH} > \text{pyridine} > \text{H}$ .

An interesting correlation in chemical shifts of the methylene protons of 2,2'-dipyridylmethane (I) and various nitrogen substituted derivatives (II-IV) was observed.



The downfield shift of the methylene protons increased in the following order: I II III IV. The downfield shift of the  $\text{BH}_2^+$  cation, as well as that of the ammonium ( $1^+$ ) salt, from the free amine was expected, based on electronic



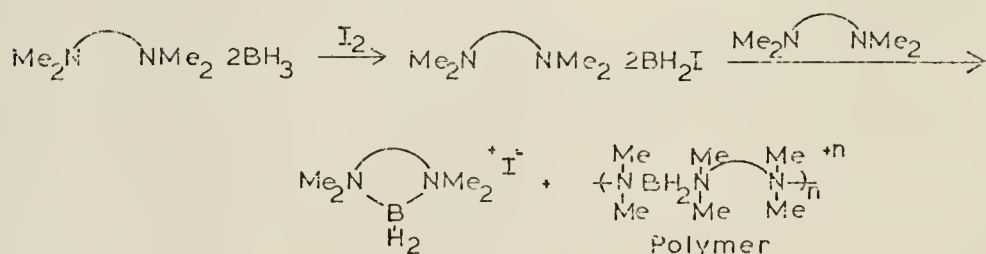
effects. The greater downfield shift of the  $\text{BH}_2^+$  cation than the ammonium (1+) salt is consistent with previously reported results.<sup>17</sup> What was surprising was the further downfield shift of the bis(borane) derivative compared to the boronium cation. This appears to be a reversal of the results obtained from other bis(boranes) and boronium cations reported in this study. However, the structure of the bis(borane) of 2,2'-dipyridylmethane is unique, since the methylene ( $\text{CH}_2$ ) group is bridged by two pyridine rings. Coordination of two electron deficient  $\text{BH}_3$  groups to the pyridine nitrogen atoms would be expected to alter the electron density of the aromatic system, providing a deshielding of the bridging methylene ( $\text{CH}_2$ ) group. Apparently, the two borane ( $\text{BH}_3$ ) groups have a greater inductive effect than the formal positive charge on the boronium cation. One interesting implication of this data is that the bis(borane) should also be susceptible to deprotonation, as was demonstrated for the boronium cation. Investigation of this reaction was not undertaken in this study, but the presence of orange solutions observed in the synthesis of the bis(borane) suggests that deprotonation is occurring. The increased reactivity of pyridine-boranes toward decomposition by alkaline aqueous solutions, and the exchange reactions with other amines, would complicate study of this reaction.

In general, there is a definite downfield chemical shift in all the proton resonances of the polyamines on

coordination to  $\text{BH}_3$  and  $\text{BH}_2^+$  groups. Resonances belonging to the pyridine ring protons were assigned on the basis of their relative intensities, multiplicity, and relative chemical shifts.<sup>47,48</sup> The  $^{11}\text{B}$  resonances appeared as quartets for amine-boranes, and triplets for the boronium ( $\text{BH}_2^+$ ) salts, and hydrogens attached to boron could not be detected in the proton spectra under normal operating conditions. As expected, there is a definite downfield shift of the boronium resonances in  $\text{BH}_2^+$ , compared to borane ( $\text{BH}_3$ ).

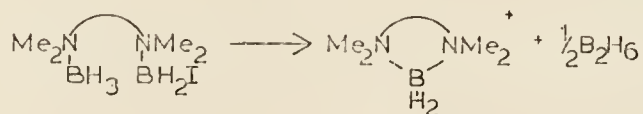
#### Critique of Reported Literature Related to This Study

In a study by Ryschkewitsch and Sullivan, it was reported that tertiary diamine-bis(boranes) could be reacted with iodine, in a quantity sufficient enough to incorporate one iodine atom on each borane group, and free diamine to yield either cyclic or linear boronium cations or mixtures of the two.<sup>26</sup>



Of particular interest was the synthesis of the five-membered, six-membered, and seven-membered aliphatic cations investigated in this study. The same authors also reported that only the five-membered ring was selectively formed

over linear cation, and only a small yield (9%) for the six-membered ring was obtained, with no seven-membered ring being observed. The apparent tendency of bis(iodo-boranes) containing more than five atoms to form linear cations is of interest, since in this study only cyclic boronium cations were observed. In their experiments, Ryschkewitsch and Sullivan reported that a dark brown solution remained one hour after the addition of iodine, suggesting the presence of unreacted iodine. That iodine remained even when a small excess of bis(borane) was employed was of interest, since the reaction of amine-boranes with iodine generally yields colorless solutions. A possible explanation for this observation can be extrapolated from the results of this study. Iodine added slowly to a bis(borane) can produce a sufficient amount of mono-iodonated bis(borane) intermediate, which can cyclize, as reported in this study, to form the cyclic cation and one-half mole of diborane.

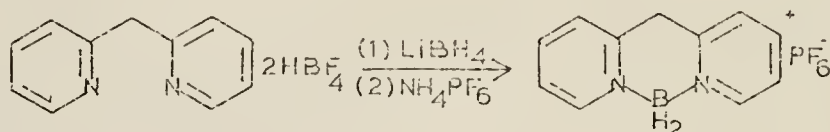


If this reaction does occur, the amount of iodine required would be reduced.

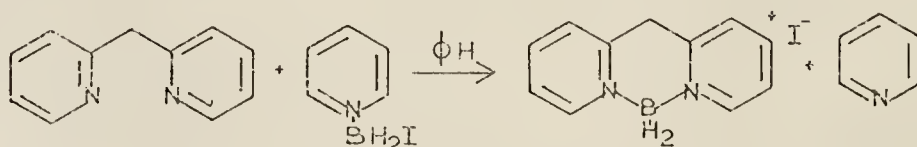
The fact that the six-membered ring cation was produced in only 9% yield, while the five-membered ring cation was produced quantitatively, correlates well with the rates

of formation observed in this study, and it is possible that the 9% yield of the six-membered ring cations results exclusively from the reaction of mono-iodinated bis(borane), as described in this study. The procedure for linear cation formation reported by Ryschkewitsch and Sullivan, and the procedure reported in this study, provides considerable control over linear or cyclic boronium cation synthesis.

As mentioned earlier, Douglass and co-workers reported concurrently with this work, the synthesis of a compound claimed to be 2,2'-dipyridylmethanedihydroboron (1+) iodide, and also the hexafluorophosphate salt.<sup>11</sup> The first of two reported methods of synthesis was the reaction of the ammonium (2+) salt ( $\text{BF}_4^-$ ) of 2,2'-dipyridylmethane, with lithium borohydride in monoglyme, at 25°C.



The second method involved the reaction of 2,2'-dipyridylmethane with pyridine-iodoborane, in benzene.



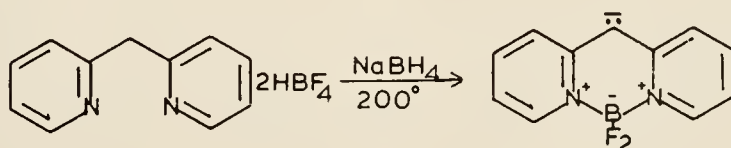
The analytical results, as well as the reported infrared and proton nmr spectra, agreed well with the assigned

structures. However, it was reported that the cation derived from either method of synthesis was quite resistant to deprotonation with trimethylamine or 1,8-bis(dimethylamino)-naphthalene, and when treated with aqueous sodium hydroxide, a fleeting red color was observed, but the only isolable product was 2,2'-dipyridylmethane. These results are in direct contradiction with those reported in this study. It is the opinion of this author that the materials reported by Douglass and co-workers are not the cyclic boronium cation of 2,2'-dipyridylmethane, and it is possible that the materials they isolated are mixtures of ammonium salts, such as those listed below:



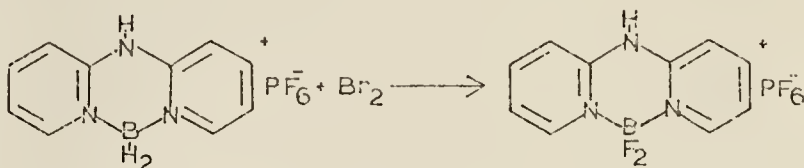
A small amount of the cyclic boronium cation or bis(borane) may have also been present, which could account for the fleeting red color reported when the materials were reacted with aqueous sodium hydroxide. The analytical, proton nmr spectrum, and infrared spectrum of a mixture of the above would be consistent with those reported.

Douglass and co-workers also reported the synthesis of a cyclic difluoro-boron zwitterion from 2,2'-dipyridylmethane by the following method.



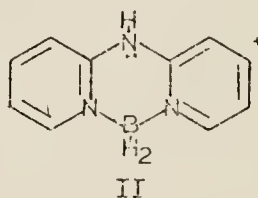
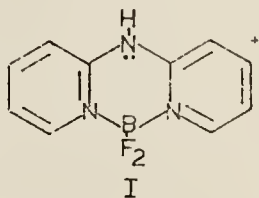
This material was shown to be protonated by acid and deproton-

ated by bases such as triethylamine. These results are in good agreement with those expected of such a material, as well as consistent with the results obtained in this study. The fluorination of the boron atom in the cyclic cation supports the results obtained by Abate, on the cyclic boronium cation of 2,2'-dipyridylamine.<sup>4</sup> Abate found that fluorination can be readily accomplished with a fluoride donor, such as  $\text{PF}_6^-$ , and it is not surprising that  $\text{BF}_4^-$  shows similar results.



Douglass and co-workers rationalized the difference in reactivity of the difluoro derivative and dihydro derivative as being an inductive effect of the fluorine atoms, thus increasing the acidity of the methylene protons.

The pKa of the difluoro-derivative (I) of the cyclic boronium cation of 2,2'-dipyridylamine was shown by Abate to decrease from a pKa of 8.2 for the dihydro-derivative (II) to a pKa of 5.0 for the difluoro-derivative.



Comparison of these two compounds with the analogous 2,2'-dipyridylmethane derivatives suggests that the difference in pKa is too slight to account for such a radical change

in the molecules reactivity as was proposed by Douglass.

At any rate, the results in this study show that the

$\text{BH}_2^+$  cation still retains considerable acidity ( $\text{pK}_a=12.13$ ).



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Larry Manziek was born in New Orleans, Louisiana, on June 11, 1946. After completing his secondary education in Pensacola, Florida, he entered Pensacola Junior College and completed his initial college studies there. In June, 1970, he received the degree Bachelor of Science with a major in Chemistry from the University of West Florida. During that time, he received The American Institute of Chemistry Award and the Monsanto Award.

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Mr. Manziek is presently employed with Rohm and Haas Company as a Senior Research Chemist, Department of Pollution Control Research.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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